Phosphorus Control in Passive Wastewater Treatment and Retention Works Using Water Treatment Residual Solids

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By

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ABSTRACT

Water treatment residual solids (WTRS) were characterized and studied as a potential phosphorus (P) adsorbent for application in sewage lagoons and stormwater runoff retention ponds. Three conventional WTRS sludge types (mixed $Fe(OH)_3$-$CaCO_3$, mixed $Al(OH)_3$-$CaCO_3$, and $Al(OH)_3$) were collected from the Saskatoon, Prince Albert, and Buffalo Pound water treatment plants (WTP), respectively. The WTRS were collected in slurry form (i.e. not dried) from WTP clarifiers. Samples were collected during the summer and fall in an effort to observe seasonal effects.

WTRS characterization involved determining selected chemical parameters which included pH, ammonium oxalate-extractable aluminum and iron content, and ammonium acetate-extractable calcium content. The pH of the WTRS samples ranged from approximately 6 to 8. Saskatoon WTRS samples had Fe_{ox} content in the range of 55.2-55.8 g kg^{-1} of dry WTRS solid. Prince Albert WTRS samples had Al_{ox} in the range of 41.8-46.7 g kg^{-1} of dry WTRS solid. Buffalo Pound had Al_{ox} content in the range of 56.0-67.2 g kg^{-1} of dry WTRS solid. Saskatoon and Prince Albert WTRS samples had Ca content ranging between 34.3-38.1 g kg^{-1} of dry WTRS solid due to lime softening. Typically the fall WTRS samples had higher Al, Fe, and Ca content than the summer WTRS samples.

Phosphorus adsorption behaviour and the maximum adsorption capacity of the WTRS were investigated through batch adsorption and settling experiments of WTRS in P-spiked deionized water. The Langmuir isotherm model best described the P adsorption behaviour of the WTRS (R^2 = 0.97-1.00 linearized transformed data). The Freundlich isotherm model had not as good a fit with R^2 ranging from 0.63 to 0.87 for the WTRS. The summer WTRS samples achieved maximum adsorption capacities (Q_{max}) in the following order: Buffalo Pound (78.1 mg P/g solid) > Prince Albert (70.4 mg P/g solid) > Saskatoon (7.37 mg P/g solid). The fall WTRS samples resulted in similar Q_{max} results in the following order: Buffalo Pound (82.0 mg P/g solid) > Prince Albert (70.4 mg P/g solid) > Saskatoon (6.41 mg P/g solid). Seasonal variations appeared to have minor impact on WTRS P adsorption.

Phosphorus removal from sewage lagoons and stormwater runoff retention ponds was examined through batch adsorption and settling experiments of WTRS. Municipal primary wastewater effluent from the Saskatoon wastewater treatment plant (WWTP) was used as a surrogate for lagoon effluent during spring discharge. Stormwater runoff was collected from an agricultural runoff pond outside Saskatoon. Aluminum and iron based WTRS were effective at adsorbing phosphorus from municipal primary wastewater effluent in batch adsorption treatment. WTRS dosages removed P to within 6.4% of their target final P concentrations. However, the WTRS were not effective at adsorbing P from agricultural runoff water. After remixing the settled WTRS and doubling the dosage in the agricultural runoff water the WTRS only removed approximately 20-25% P.

Re-suspension and resettling of WTRS after an initial cycle of P adsorption and settling had negligible effect upon the P concentration in the water column. The WTRS had a negligible effect on the pH of the wastewater solutions at the dosed concentrations. Short term (14 days) desorption of P from the WTRS utilized in P adsorption tests was low, typically less than 2% and reaching as high as 10.6% of the total P adsorbed.

WTRS were found to be an effective P adsorbent from municipal primary wastewater effluent. The WTRS had high adsorption capacities compared to other WTRS and P adsorbents in the literature. The high adsorption capacities of the Al-based WTRS make them more practical than Fe-based WTRS for application.

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LIST OF SYMBOLS/TERMINOLOGY

amu	Atomic mass unit
Al	Aluminum
$Al(OH)_3$	Aluminium hydroxide
Al_{ox}	Oxalate-extractable aluminum
BET	Brunauer-Emmett-Teller
BOD	Biological oxygen demand
BOD_5	Biological oxygen demand over a 5 day period
BP	Buffalo Pound
C_0	Initial phosphorus concentrations
Ca	Calcium
$CaCO_3$	Calcium carbonate
C_e	Equilibrium phosphorus concentration
COD	Chemical oxygen demand
Fe	Iron
$Fe(OH)_3$	Iron hydroxide
Fe_{ox}	Oxalate-extractable iron
k	Langmuir equilibrium constant
K_f	Freundlich equilibrium constant
N	Nitrogen
OP	Orthophosphate
P	Phosphorus
PA	Prince Albert
PO_4^{3-}	Orthophosphate (phosphate)
Q	Adsorption density at equilibrium (amount of adsorbed phosphorus per unit weight of adsorbent)
Q_{max}	Theoretical maximum adsorption density
SK	Saskatoon
TDP	Total dissolved phosphorus
TKN	Total Kjeldahl nitrogen

TN	Total nitrogen
TP	Total phosphorus
TS	Total solids
TSS	Total suspended solids
WTP	Water treatment plant
WTRS	Water treatment residual solid
WWTP	Wastewater treatment plant

CHAPTER 1 Introduction

1.1 Background

Water treatment residual solids (WTRS) are waste products from the surface water treatment process. A typical water treatment plant (WTP) that treats surface waters involves coagulation, flocculation, sedimentation, and filtration to remove suspended solids from the source water. The residual solids produced from these processes typically contain minerals and humic material precipitated from the source water, aluminum or iron hydroxide precipitates from coagulation, calcium carbonate precipitates (if lime softening is performed), microbes, chemicals from other stages of treatment, and chemical species that were removed from the source water (e.g. arsenic, aluminum, and iron). Water treatment plants produce large quantities of WTRS and typically process the residuals rather than discharging them back into the source water. A common technique is to dewater and then landfill the residuals. However, some practical uses of residual solids are being explored.

Phosphorus (P) is a ubiquitous element in the environment and is a limiting nutrient in aquatic systems. Aquatic plants require phosphorus, however excess phosphorus can cause eutrophication which can lead to increased algal growth and associated degradation of water quality. The largest contributors of P to fresh water systems are domestic wastewater effluent discharge (point source) and agricultural and urban runoff (non-point source). Domestic wastewater effluent discharge is typically where P reduction efforts are imposed since it is easier to control point sources compared to non-point sources (Corbridge 2000).

Conventional secondary wastewater treatment plants typically use biological and chemical processes to remove phosphorus from wastewater. In Saskatchewan the objective for P in effluents being discharged to receiving streams is 1 mg/L as total phosphorus (Saskatchewan Ministry of Environment 2008). Small scale wastewater sources, such as sewage lagoons and stormwater retention ponds, typically do not have advanced P removal treatment technologies and may not be able to achieve the phosphorus objective. Adsorption of phosphorus by WTRS has been shown to be an effective method for removing phosphorus from domestic wastewater

(Babatunde and Zhao 2010; Gibbons 2009; Razali et al. 2007; Yang et al. 2006a,b; Dayton and Basta 2005a; Makris et al. 2005a; Dayton et al. 2003; Ippolito et al. 2003; Kim et al. 2003; Huang and Chiswell 2000; Galarneau and Gehr 1997). Water treatment residuals may have potential for phosphorus removal via batch adsorption and settling in sewage lagoons and stormwater runoff retention ponds.

1.2 Research Objectives

The objective of this research was to investigate the use of water treatment residual solids for immobilization of soluble phosphorus and prevention of phosphorus movement to the environment within effluents from wastewater lagoons and stormwater runoff retention ponds. The main objective was investigated through the following three sub-objectives:

1. Verify the chemical characteristics of typical WTRS reported by other researchers;
2. Explore the use of acid ammonium oxalate extractable aluminum (Al_{ox}) and iron (Fe_{ox}) as a substitute for adsorption isotherm testing to estimate the maximum adsorption capacity; and
3. Investigate the use of WTRS for phosphorus control in passive wastewater treatment and retention works (lagoons and stormwater runoff retention ponds) using laboratory batch adsorption and settling tests.

These objectives were investigated through the following tasks:

1. Determining selected chemical parameters of unaltered, non-dried, clarifier sludge water treatment residual solids which included pH, ammonium oxalate-extractable aluminum and iron content, and ammonium acetate-extractable calcium content;
2. Batch adsorption and settling experiments of unaltered, non-dried, clarifier sludge WTRS in phosphate-spiked deionized water to study the phosphorus adsorption behaviour and determine the maximum adsorption capacity of WTRS;
3. Batch adsorption and settling experiments of unaltered, non-dried, clarifier sludge WTRS in municipal primary wastewater effluent (a surrogate for lagoon effluent during spring

discharge) and stormwater runoff water to study phosphorus removal by adsorption on WTRS and settling within effluents; and

4. Desorption experiments of unaltered, non-dried P-loaded clarifier sludge WTRS to evaluate the short term (14 days) stability of phosphorus adsorption-bonding on WTRS.

1.3 Scope

The scope of the study was to characterize (measure selected chemical characteristics of) typical WTRS and to investigate P removal by adsorption using WTRS in batch simulations of passive wastewater treatment and stormwater runoff retention works.

The water treatment residual solids investigated were limited to:

1. Three conventional water treatment plant sludge types (mixed $Fe(OH)_3$-$CaCO_3$, mixed $Al(OH)_3$-$CaCO_3$, and $Al(OH)_3$) collected from three WTPs within Saskatchewan;
2. Two different collection periods at each WTP to observe WTRS seasonal variation;
3. Sludge collected from WTP clarifiers during a clarifier blowdown (sludge pumping cycle); and
4. The slurry form in which the WTRS were collected (i.e. the solids were only allowed to settle, but were not dried or sieved) before use in the study.

The characterization of water treatment residual solids was limited to:

1. Measurements of Al, Fe, and Ca content and pH;
2. Measurements of P adsorption behaviour and determination of maximum P adsorption capacity through batch adsorption experiments in phosphate-spiked deionized water at representative domestic wastewater effluent P concentrations with no pH adjustment;
3. No physical characterizations of the WTRS such as particle size distribution, porosity, or surface area; and
4. No exploration of particle size, pH, age, or temperature effects on WTRS P adsorption.

The investigation of P removal by adsorption using WTRS in passive wastewater treatment and retention works was limited to:

1. Phosphorus removal treatment by adsorption using WTRS in municipal primary wastewater effluent (a surrogate for lagoon effluent during spring discharge) and stormwater runoff pond water with no pH adjustment;
2. Observations of the effects of re-suspending settled WTRS in the wastewater samples;
3. Short term (14 days) stability of adsorbed P investigation through desorption experiments of P-loaded WTRS mixed in deionized water; and
4. No exploration of particle size, pH, age, or temperature effects on WTRS P adsorption.

1.4 Significance of Research

The distinct contributions of this research to water and wastewater engineering are:

1. An investigation of the phosphorus adsorption characteristics of unaltered, non-dried water treatment residual solids collected directly from clarifiers in slurry form; and
2. An investigation of the application of the collected WTRS in slurry form for phosphorus removal by batch adsorption and settling in municipal wastewater and stormwater runoff.

The application of WTRS waste slurry material for control of P from passive wastewater treatment and retention works could potentially improve the water quality of the wastewater effluent discharged and the receiving bodies of water. Sewage lagoons and stormwater runoff ponds that may lack P removal capabilities and struggle to meet regulatory phosphorus guidelines could benefit from using WTRS for P control by adsorption and settling. The WTRS slurry would be inexpensive, accessible, and easy to apply. Recycling of WTRS slurry would also reduce the loading to landfills or to surface water sources (if the WTRS are being discharged back into the source water).

CHAPTER 2 Literature Review

2.1 Phosphorus

Phosphorus (P) is a non-metallic element which has the atomic number 15 and atomic weight 30.974 amu. It is a ubiquitous element within living cells and the surrounding environment. Phosphorus is highly reactive, especially under oxidizing conditions, and never found in free form in nature but almost always in its fully oxidized state as phosphate (PO_4^{3-}) (Corbridge 2000). A significant source of P in the environment is from phosphate rock which contains the impure tri-calcium phosphate mineral apatite (Environment Canada 2004). Typical quantities of P in the environment are shown in Table 2.1.

Table 2.1 Typical quantities of phosphorus in the environment (adapted from Corbridge 2000)

Environmental Source	Weight % P
Air	< 0.00
Phosphate rock	10.5 - 15.0
Plants	0.05 - 0.5
Rain water	0 - 0.001
Sea water	0.0001 - 0.001
Soil	0.02 - 0.5

2.1.1 Phosphorus Chemistry

Due to the reactivity of phosphate it bonds with many cations such as iron (Fe), aluminum (Al), and calcium (Ca) which form relatively insoluble compounds. The most common P compounds are oxyphosphorus compounds all of which contain phosphorus - oxygen connections (Corbridge 2000). Oxyphosphorus compounds include orthophosphates, condensed phosphates, and organic phosphate esters (phosphorus - oxygen - carbon bonds). Common classes of phosphorus-containing compounds in aquatic systems are shown in Table 2.2.

Table 2.2 Classes of phosphorus containing compounds of importance in aquatic systems (from Snoeyink and Jenkins 1980)

Group	Species of Importance	Acid Ionization Constants (25°C)
Orthophosphate	H_3PO_4, $H_2PO_4^-$,	$pK_{a1} = 2.1$
	HPO_4^{2-}, PO_4^{3-},	$pK_{a2} = 7.2$
	HPO_4^{2-} complexes	$pK_{a3} = 12.3$
Polyphosphates		
Pyrophosphate	$H_4P_2O_7$, $H_3P_2O_7^-$,	$pK_{a1} = 1.52$
	$H_2P_2O_7^{2-}$,	$pK_{a2} = 2.4$
	$HP_2O_7^{3-}$, $P_2O_7^{4-}$,	$pK_{a3} = 6.6$
	$HP_2O_7^{3-}$ complexes	$pK_{a4} = 9.3$
Tripolyphosphate	$H_3P_3O_{10}^{2-}$,	$pK_{a3} = 2.3$
	$H_2P_3O_{10}^{3-}$,	$pK_{a4} = 6.5$
	$HP_3O_{10}^{4-}$, $P_3O_{10}^{5-}$,	$pK_{a5} = 9.2$
	$HP_3O_{10}^{4-}$ complexes	
Metaphosphates	$HP_3O_9^{2-}$, $P_3O_9^{3-}$	$pK_{a3} = 2.1$
Organic phosphates	Very many types, including phospholipids, sugar phosphates, nucleotides, phosphoamides, etc.	

Equilibrium reactions for orthophosphates in water are (Stumm and Morgan 1995):

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-; \qquad pK_{a1} = 2.1 \qquad [2.1]$$

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}; \qquad pK_{a2} = 7.2 \qquad [2.2]$$

$$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}; \qquad pK_{a3} = 12.3 \qquad [2.3]$$

The dominant form of orthophosphate present in water is controlled by the pH of the solution (Stumm and Morgan 1995) as shown in Figure 2.1.

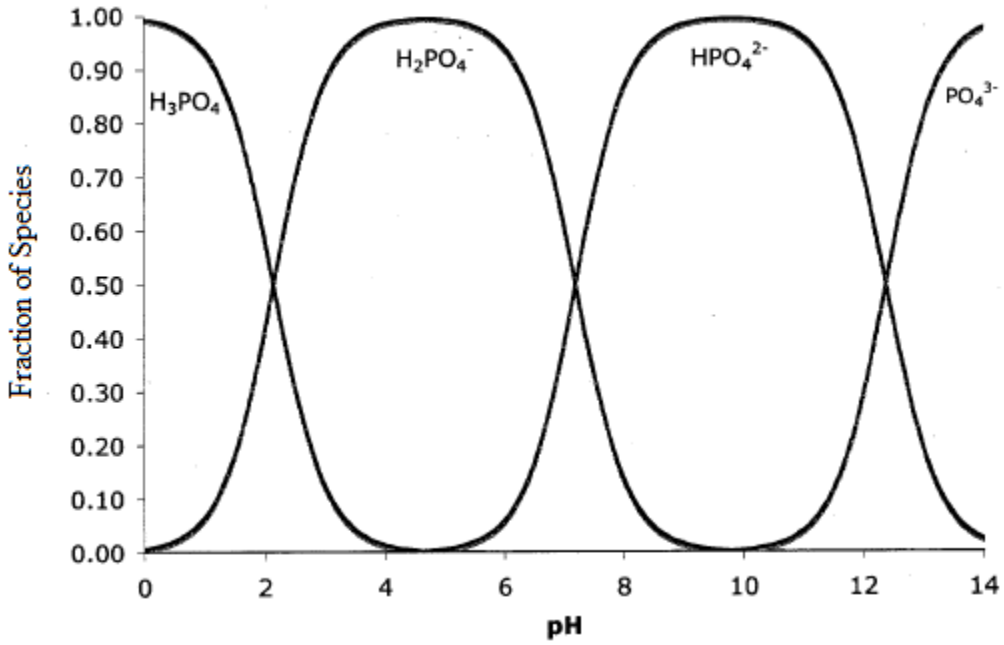

Figure 2.1 Phosphate distribution in water of varying pH (from Gibbons 2009)

2.1.2 Phosphorus in Aquatic Systems

In aquatic systems P occurs in three forms: inorganic P, particulate organic P, and dissolved (soluble) organic P. Aquatic plants require inorganic P, typically as PO_4^{3-}, for nutrition. As much as 95% of P in fresh water occurs as organic phosphates, components of cells within organisms, and within or adsorbed to inorganic and dead particulate organic material (Environment Canada 2004). Phosphorus enters fresh water from atmospheric precipitation, point sources such as wastewater treatment plants, and non-point sources such as stormwater and agricultural runoff. The phosphorus cycle is shown in Figure 2.2.

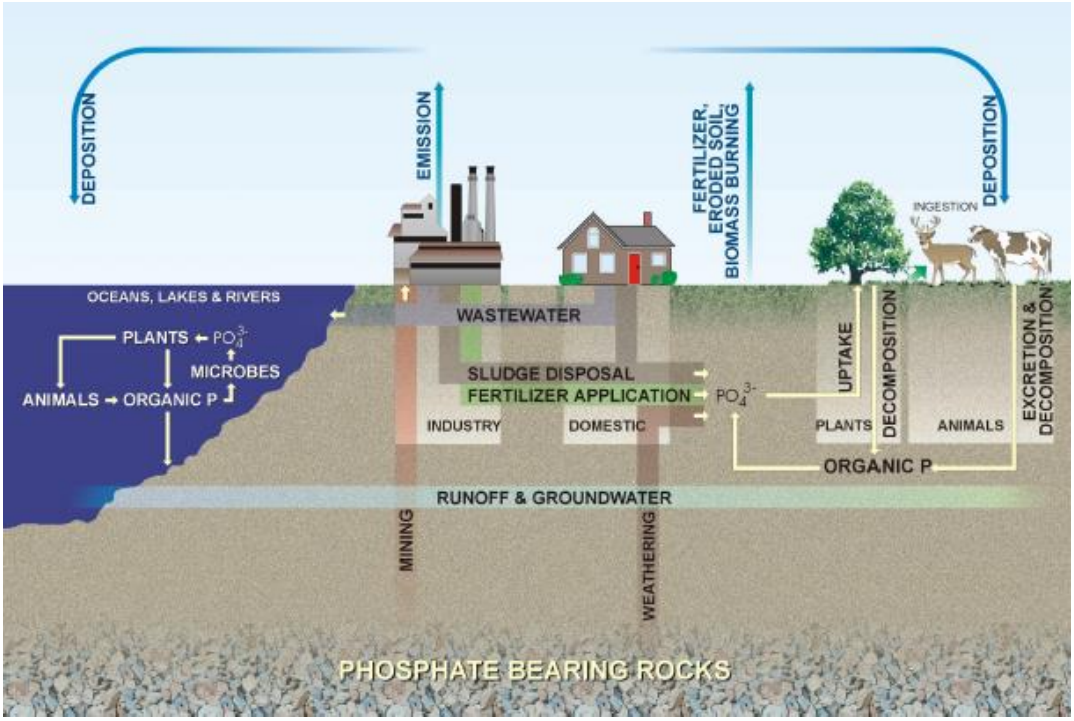

Figure 2.2 Phosphorus cycle in the environment (from Chambers et al. 2001)

Excess nutrients, specifically N and P, in lakes can cause eutrophication which can lead to increased algal growth. Excessive algae can interfere with the photosynthetic process of rooted aquatic plants by blocking sunlight and carbon dioxide flow. Further, increased algal growth can lead to dissolved oxygen depletion in water bodies during algal respiration periods and as a result of aerobic microbial biodegradation of dead algal cells (WRI 2013).

The two largest contributors to excess nutrients in aquatic systems are agricultural runoff and domestic wastewater (Corbridge 2000). High P concentrations in agricultural runoff typically arise from increased fertilizer use while human excrement and increased detergent use contribute to high P concentrations in domestic wastewater. Typical phosphorus levels in aqueous systems are shown in Table 2.3. Since domestic wastewater is a point source of pollution opposed to agricultural runoff being a non-point source, it is typically where P reduction efforts are imposed since point sources are easier to control (Corbridge 2000).

Table 2.3 Typical nutrient levels in aqueous systems (adapted Corbridge 2000)

Water Source	N (mg/L)	P (mg/L)
Agricultural drainage water	10	1
Domestic wastewater	40	10
Treated sewage effluent	30	5
Rain water	0.01	0.001
Lake water (with nutrient input)	0.3	0.03
River water	5	1

2.1.3 Phosphorus Regulations

There are no national environmental quality guidelines for phosphorus for Canada; however, provinces may have individual guidelines or objectives (Environment Canada 2004). The objectives for Saskatchewan for all waters receiving effluents are to be free from substances in concentrations or combinations which are acutely toxic or may be harmful to human, animal, or aquatic life and to be free from nutrients in concentrations that create nuisance growths of aquatic weeds or algae or that results in an unacceptable degree of eutrophication in the receiving water (Saskatchewan Environment 2006a). In terms of wastewater treatment where phosphorus control is undertaken for nutrient removal purposes, the process should be designed and operated to meet an effluent objective of 1 mg/L as total phosphorus or to conform to any required mass loading limitation (Saskatchewan Ministry of Environment 2008).

The levels and forms of phosphorus present in the environment are non-toxic to aquatic life but can cause eutrophication. The effects of phosphorus are not purely negative therefore aquatic systems adapt to different conditions. The management goals and objectives as well as the water quality and desired uses of the water system are important factors when determining an acceptable phosphorus content level. It is therefore difficult, and not reasonable, to have a single guideline value for phosphorus in freshwater systems. A phosphorus guidance framework and trigger ranges (Table 2.4) has been established to assist in setting local guidelines and to determine the potential for phosphorus concentration in water bodies to cause adverse environmental effects.

Table 2.4 Total phosphorus trigger ranges for Canadian lakes and rivers (Environment Canada 2004)

Trophic Status	Canadian Trigger Ranges Total Phosphorus (µg/L)
Ultra - oligotrophic	< 4
Oligotrophic	4 - 10
Mesotrophic	10 - 20
Meso - eutrophic	20 - 35
Eutrophic	35 - 100
Hyper - eutrophic	> 100

2.1.4 Analytical Characterization of Phosphorus

Characterizing the various forms of phosphorus is dependent upon the filtration and chemical methods of analysis. Filtration methods are used to differentiate dissolved P and particulate P. Filtering samples through 0.45 µm pore diameter membrane filters separates dissolved P from suspended P. However this filtration procedure is not necessarily a true separation but a convenient and replicable analytical technique (APHA-AWWA-WEF 2005). Inorganic and organic phosphorus are differentiated by chemical methods. Three chemical types (Table 2.5), reactive, acid-hydrolyzable, and organic phosphorus, analytically describe the total phosphorus as well as the dissolved and suspended phosphorus fractions (APHA-AWWA-WEF 2005). Typically, the unfiltered and filtered P fractions are determined analytically, while the suspended fractions may be determined by the difference. When determining forms of phosphorus it is important to state the filtration and chemical methods used as the phosphorus estimate will vary based on the different methods.

Table 2.5 Definition of phosphorus fractions (from APHA-AWWA-WEF 2005)

Phosphorus Fraction	Definition
Reactive	- Phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample - Largely a measure of orthophosphate - Occurs in both dissolved and suspended forms
Acid-hydrolyzable	- Dissolved and particulate condensed phosphates converted to dissolved orthophosphate by acid hydrolysis at boiling water temperature - Occurs in both dissolved and suspended forms
Organic	- Phosphate fractions that are converted to orthophosphate only by oxidation destruction of the organic matter present - Occurs in both dissolved and suspended forms

2.2 Municipal Wastewater

Municipal sewer systems serviced 73% of Canadians in 1996 (Chambers et al. 2001). At least 94% of the sewage collected by sewer systems received primary treatment or better (Chambers et al. 2001) while the majority of sewage in the interior of the country received secondary treatment or better. The remaining 6% was serviced by collection systems that discharged untreated wastewater directly into lakes, rivers, or oceans (Chambers et al. 2001). Typical effluent quality at various levels of treatment are shown in Table 2.6.

Table 2.6 Typical effluent quality of sewage treatment processes (from Saskatchewan Ministry of Environment 2008)

Process	BOD_5 (mg/L)	TSS (mg/L)	Total P (mg/L)	Total N (mg/L)	Total Coliforms/ 100 mL
Primary					
(including anaerobic lagoons)	75 - 150	50 - 110	5 - 7	25 - 45	$> 2x10^6$
with phosphorus removal	45 - 85	25 - 50	1 - 2	20 - 40	$> 2x10^5$
Secondary					
Biological (mechanical)	10 - 25	10 - 25	3.5 - 6.5	15 - 35	$2x10^4$ - $2x10^5$
Aerated lagoons	15 - 30	20 - 35	4 - 7	20 - 40	$2x10^3$ - $2x10^5$
Facultative lagoons					
- Spring	25 - 70	20 - 60	3.5 - 7	20 - 35	$< 2x10^3$ - $2x10^5$
- Late Fall	10 - 30	10 - 40	2 - 5	5 - 20	$2x10^2$ - $2x10^4$
Advanced					
Secondary with chemical treatment (phosphorus control)	5 - 15	10 - 30	0.5 - 1.5	15 - 35	$2x10^2$ - $2x10^4$

2.2.1 Phosphorus Removal Technologies in Municipal Wastewater Treatment Plants

Biological and chemical processes can be utilized to remove phosphorus from wastewater. Some wastewater treatment plants may use both methods. Conventional secondary biological wastewater treatment processes do not remove phosphorus effectively (U.S. EPA 2008).

2.2.1.1 Biological Treatment for Phosphorus Removal

The biological removal of phosphorus involves anaerobic and aerobic processes. The anaerobic biological phosphorus release by Phosphate Accumulating Organisms (PAOs) reaction (U.S. EPA 2008) is:

$$\text{PAOs + stored polyphosphate + } Mg^{++} + K^{+} \text{ glycogen + VFA} \rightarrow \text{PAOs + stored biopolymers + } Mg^{++} + K^{+} + \_CO_2 + H_2O + PO_4^{3-} \text{ (released)} \quad [2.4]$$

The aerobic biological phosphorus uptake by PAOs reaction (U.S. EPA 2008) is:

$$\text{PAOs + stored biopolymers + } Mg^{++} + K^{+} + O_2 \text{ (or } NO_3) + PO_4^{3-} \rightarrow \text{PAOs + stored polyphosphate + } Mg^{++} + K^{+} + \text{glycogen + } CO_2 + H_2O \quad [2.5]$$

Phosphate is released in anaerobic conditions when PAOs break the bonds of internally accumulated polyphosphate. In aerobic conditions PAOs take up phosphate in greater amounts than what was released. The PAO phosphate uptake is removed when the microorganisms are separated from the system by clarification. Some phosphate is also removed by microorganisms when they remove BOD. Factors influencing the efficiency of biological phosphorus removal include volatile fatty acid availability in wastewater, temperature, and solids retention time (U.S. EPA 2008).

2.2.1.2 Chemical Treatment for Phosphorus Removal

Chemical phosphorus removal occurs by chemical precipitation. Trivalent metal cations such as Al^{3+}, added with alum (aluminum sulphate), and Fe^{3+}, in the form of ferric chloride ($FeCl_3$), are used to precipitate orthophosphate. Various phosphate species are converted to PO_4^{3-} with the consumption of alkalinity (U.S. EPA 2008).

The conversion of phosphate species to phosphate ion reaction occurs by (U.S. EPA 2008):

$$H_nPO_4^{(3-n)-} + nOH^- \rightarrow PO_4^{3-} + nH_2O \quad [2.6]$$

Alum chemically removes phosphorus by (U.S. EPA 2008):

$$Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3(SO_4)^{2-} \quad [2.7]$$

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_{4\,(s)} \quad [2.8]$$

Phosphate removal from wastewater by precipitation of $AlPO_{4\,(s)}$ is most efficient at approximately pH 5.5 (Figure 2.3) (Snoeyink and Jenkins 1980). Phosphate removal may also occur by adsorption onto or incorporation into $Al(OH)_{3\,(s)}$ which is not considered in Figure 2.3. If $Al(OH)_{3\,(s)}$ precipitates in addition to $AlPO_{4\,(s)}$ then more alum is required for phosphate removal.

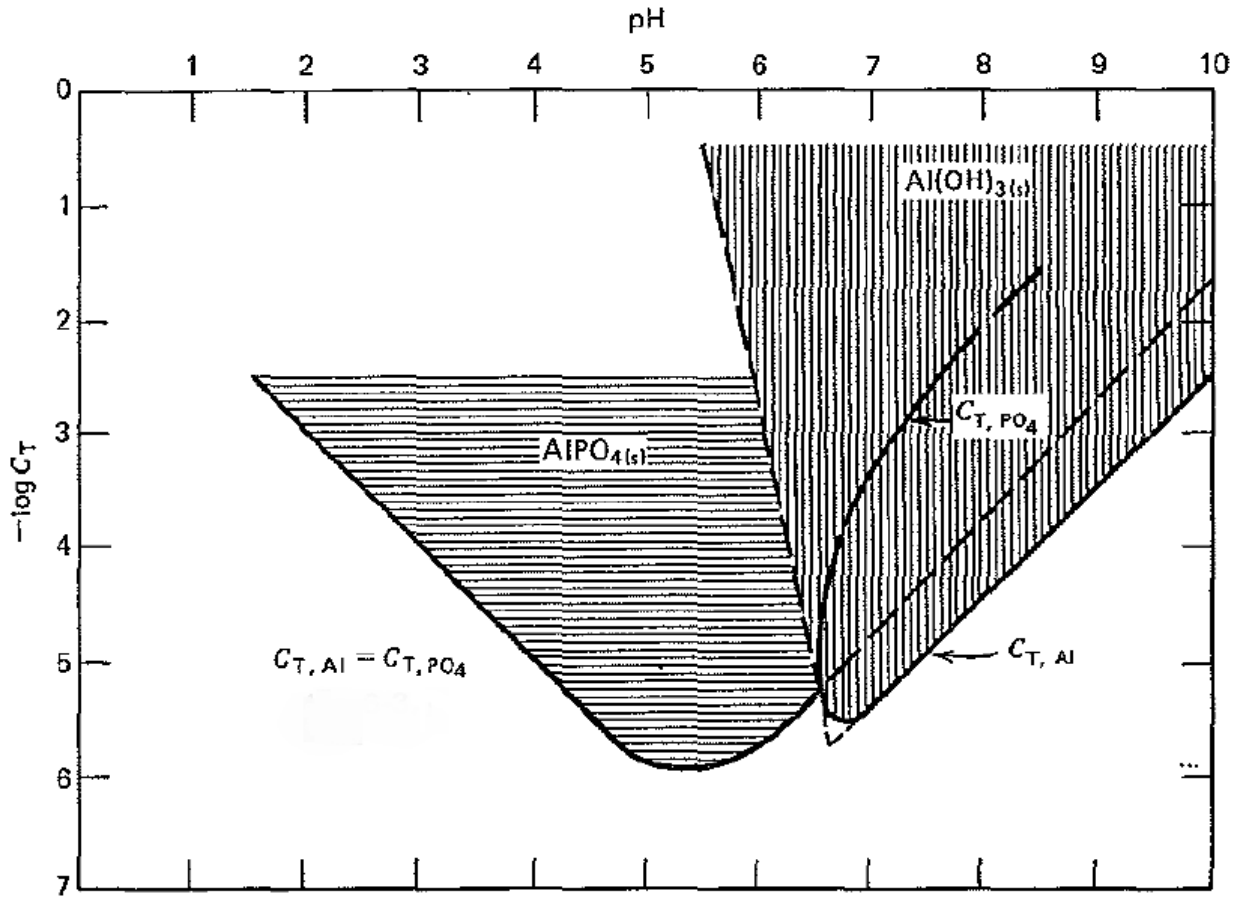

Figure 2.3 Concentration of phosphate and aluminum that can exist at various pH values when $AlPO_{4\,(s)}$ is precipitated from or dissolved in pure water (from Snoeyink and Jenkins 1980)

Ferric chloride chemically removes phosphorus by (U.S. EPA 2008):

$$FeCl_3 \rightarrow Fe^{3+} + 3Cl^- \quad [2.9]$$

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_{4\,(s)} \quad [2.10]$$

Phosphate removal can also occur by calcium phosphate precipitation. However the calcium phosphate system is complex. A variety of solids may form as shown in Table 2.7. The basic concept of the nature of calcium phosphate precipitation is shown in Figure 2.4.

Table 2.7 Representative heterogeneous and complexation equilibria of phosphates with calcium (adapted from Snoeyink and Jenkins 1980)

Heterogeneous Equilibria		pK_{so}
Calcium hydrogen phosphate	$CaHPO_{4\,(s)} \leftrightarrow Ca^{2+} + HPO_4^{2-}$	+ 6.66
Calcium dihydrogen phosphate	$Ca(H_2PO_4)_{2\,(s)} \leftrightarrow Ca^{2+} + 2H_2PO_4^-$	+ 1.14
Hydroxyapatite	$Ca_5(PO_4)_3OH_{\,(s)} \leftrightarrow 5Ca^{2+} + 3PO_4^{3-} + OH^-$	+ 55.9
β-Tricalcium phosphate	$\beta\text{-}Ca_3(PO_4)_{2\,(s)} \leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	+ 24.0
Complexation Equilibria		**pK**
With orthophosphate	$CaHPO_4^0 \leftrightarrow Ca^{2+} + HPO_4^{2-}$	+ 2.2
	$CaH_2PO_4^+ \leftrightarrow Ca^{2+}\ HPO_4^{2-} + H^+$	− 5.6
With pyrophosphate	$CaP_2O_7^{2-} \leftrightarrow Ca^{2+} + P_2O_7^{4-}$	+ 5.6
	$CaHP_2O_7^- \leftrightarrow Ca^{2+} + HP_2O_7^{3-}$	+ 2.0
With tripolyphosphate	$CaP_3O_{10}^{3-} \leftrightarrow Ca^{2+} + P_3O_{10}^{5-}$	+ 8.1

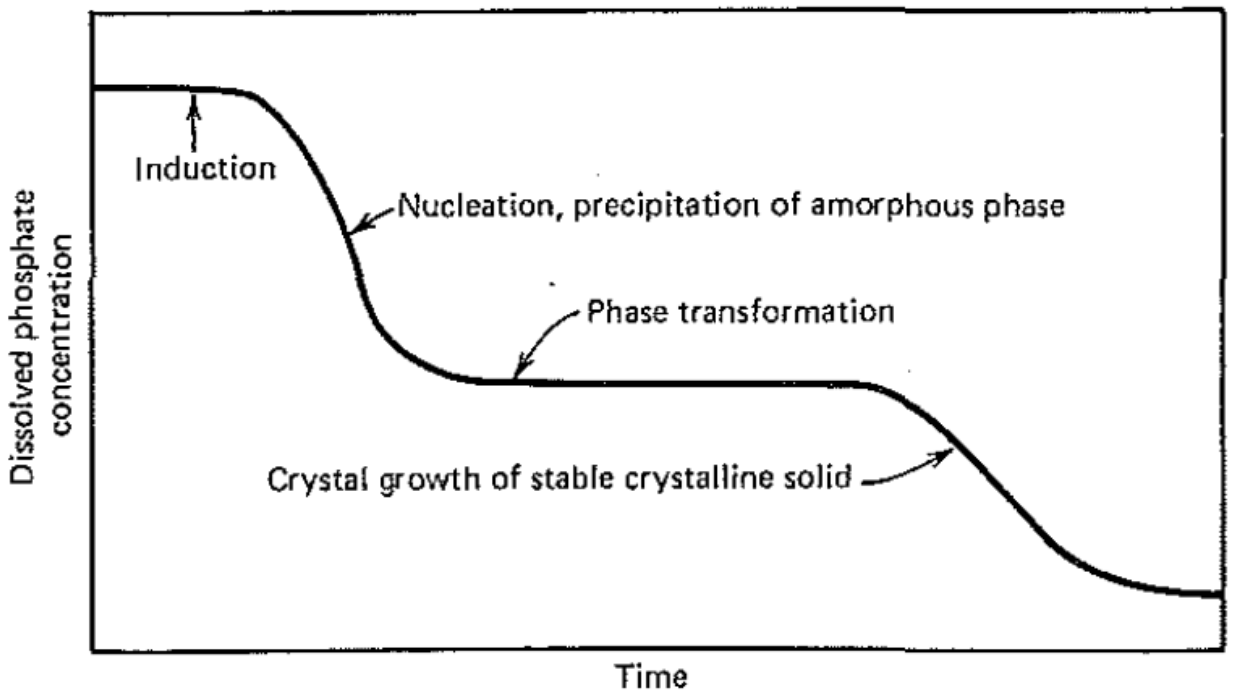

Figure 2.4 Idealized scheme for calcium phosphate precipitation kinetics (from Snoeyink and Jenkins 1980)

$FePO_{4\,(s)}$ and $AlPO_{4\,(s)}$ are the stable solid phases if phosphate is precipitated in the low pH range (below approximately pH 6). The minimum $AlPO_{4\,(s)}$ solubility occurs at about 1 pH unit higher than that of $FePO_{4\,(s)}$ (Stumm and Morgan 1995) (Figure 2.5). Metastable hydroxophosphate Al(III) or Fe(III) precipitates can be formed in the neutral pH range (Stumm and Morgan 1995).

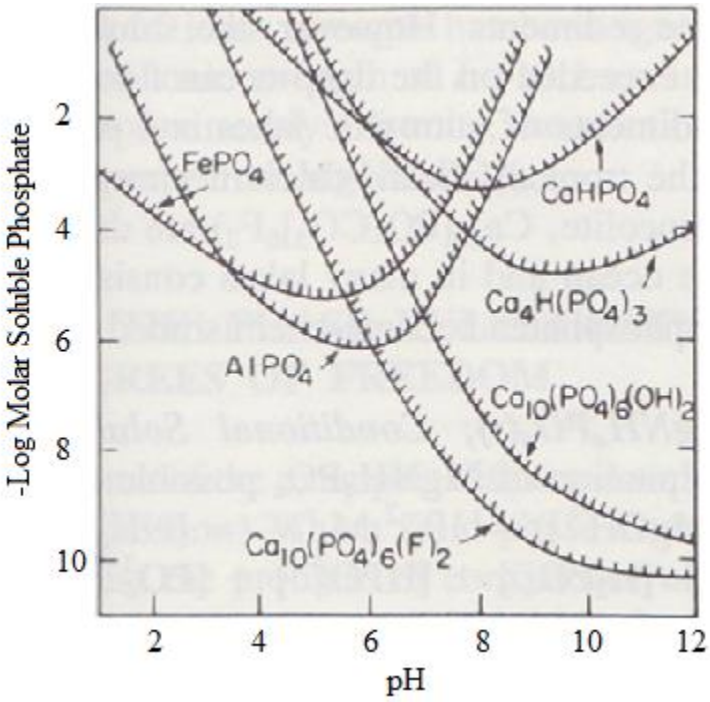

Figure 2.5 Solubility of the metal phosphates (from Stumm and Morgan 1995)

Chemical addition typically occurs in the primary or tertiary clarifiers or in the secondary process. Factors influencing chemical phosphorus removal are the phosphorus species at the application point, the choice of chemical, the feed point location and number of feed points, mixing, and pH (U.S. EPA 2008). Filtration can be used downstream of chemical addition to remove phosphate associated with suspended solids.

2.2.2 Wastewater Lagoons

In 1992, approximately 2% of Canada's population treated their wastewater with lagoons (Chambers et al. 2001). Lagoons are a significant portion of the number of treatment facilities (Table 2.8) and continue to be constructed to serve smaller communities since they are simple

and inexpensive to operate and maintain. However, by volume lagoons represent a smaller percentage of treated wastewater (InfraGuide 2004).

Table 2.8 Lagoon use in Canada in 1985 (from InfraGuide 2004)

Location	Number of Lagoons	As a Percent of Treatment Facilities
Alberta	278	84
British Columbia	34	31
Manitoba	127	85
New Brunswick	58	63
Newfoundland	1	2
Northwest Territories	15	71
Nova Scotia	14	16
Ontario	128	33
Prince Edward Island	17	9
Quebec	59	21
Saskatchewan	129	92
Yukon Territory	8	70
Canada	868	48

2.2.2.1 Lagoon Treatment Process

A lagoon is a shallow excavation in the ground where wastewater is received, held, and treated. Lagoons are less effective in colder climates. The retention time of wastewater in typical facultative lagoons is in the order of 180 days. Due to the long retention time a sludge layer develops at the bottom of a lagoon where anaerobic conditions exist. Aeration occurs naturally by diffusion on the surface as well as released by algae during its photosynthetic period. Bacteria that require oxygen decompose the organic wastes and release carbon dioxide while algae require carbon dioxide and produce oxygen. A schematic of the treatment process in a facultative lagoon is shown in Figure 2.6.

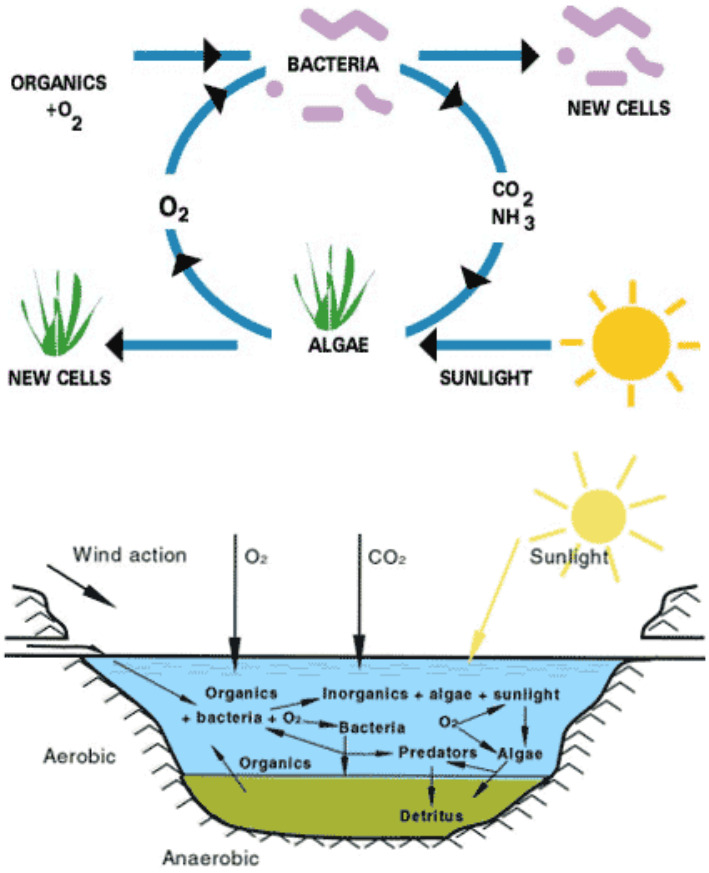

Figure 2.6 Symbiotic relationship between bacteria and algae in a wastewater lagoon (from United Nations Environment Programme 2000)

There are three types of lagoon conditions that may occur depending on the oxygen demand of the bacteria as shown in Table 2.9.

Table 2.9 Lagoon conditions based on the oxygen demand of bacteria (adapted from United Nations Environment Programme 2000)

Anaerobic lagoon	The oxygen demand of the bacteria exceeds oxygen supply by surface aeration and algal photosynthesis. Biodegradation of the organic wastes is by anaerobic bacteria. Methane gas is a by-product. Odorous gases are produced, but impact is reduced when a layer of scum forms at the water surface.
Facultative lagoon	The oxygen demand of the bacteria is met by surface aeration and algal photosynthesis, but is not met when the latter is not active. The water environment is aerobic during the day, but turns anaerobic at night. Biodegradation of organic wastes is by facultative bacteria, which can operate under both aerobic and anaerobic conditions.
Aerobic lagoon	The oxygen demand of the bacteria is met by surface aeration and algal photosynthesis.

Lagoons can also be mechanically aerated where oxygen is added to the wastewater by an aeration system or the wastewater is mixed with air from the surface. These lagoons require more energy input and labour but less land area. Table 2.10 displays some key design parameters for lagoons.

Table 2.10 Typical design parameters for lagoons (from U.S. EPA 1983a)

Pond Type	Application	Typical Loading Parameters	Typical Detention Times	Typical Dimensions	Comments
Facultative	• Raw municipal wastewater • Effluent from primary treatment, trickling filters, aerated ponds, or anaerobic ponds	22-67 kg BOD_5/ha/d	25-180 d	1.2-2.5 m deep 4-60 ha	• Most commonly used waste stabilization pond type • May be aerobic through entire depth if lightly loaded
Aerated	• Industrial wastes • Overloaded facultative ponds • Situations where limited land area is available	8-320 kg BOD_5/1000 m^3/d	7-20 d	2-6 m deep	• Use may range from a supplement of photosynthesis to an extended aeration activated sludge process • Requires less land area than facultative
Aerobic	• Generally used to treat effluent from other processes, produces effluent low in soluble BOD_5 and high in algae solids	85-170 kg BOD_5/ha/d	10-40 d	30-45 cm deep	• Application limited because of effluent quality • Maximizes algae production and (if algae is harvested) nutrient removal • High loadings reduce land requirements
Anaerobic	• Industrial wastes	160-800 kg BOD_5/1000 m^3/d	20-50 d	2.5-5 m deep	• Odor production usually a problem • Subsequent treatment normally required

2.2.2.2 Phosphorus Levels and Removal in Wastewater Lagoons

Typical total phosphorus levels in lagoons are 1 to 7 mg P/L (Table 2.6) (Saskatchewan Ministry of Environment 2008). Without specific phosphorus removal processes, aerated and facultative lagoons typically achieve lower P concentrations compared to anaerobic lagoons (Saskatchewan Ministry of Environment 2008). Lagoons typically have difficulties achieving the 1 mg/L total phosphorus objective for effluent (Table 2.6). Chemicals, particularly alum, can be added to lagoon wastewater to reduce phosphorus however it will increase the amount of sludge that is accumulated in the lagoon and increase the frequency of desludging (InfraGuide 2004). The chemicals are typically added from a motorboat. With chemical addition there would be increased labour costs for application (Table 2.11) as well as costs associated with maintenance, storage, and the chemicals. Post-treatment of effluent can also be performed to improve effluent quality, specifically phosphorus concentration. However, this also incurs more costs and requires more skillful operators (InfraGuide 2004).

Table 2.11 Labour requirements for full scale batch chemical treatments of lagoons (from Graham and Hunsinger n.d.)

	Man-hours per Acre	Man-hours per Million Gallons	Man-hours for Set-up and Clean Up per Application
Alum, liquid	2	1.6	16
Ferric chloride,			
Liquid	1.5	1.2	16
Powder	13	9.6	16
Lime,			
Dry chemical method	24	17.7	125
Haliburton method	1.7	1.4	16

2.3 Urban Stormwater

The leading water quality problem in the United States is non-point source pollutants (Zaimes and Schultz 2002). Sediment and nutrients, specifically phosphorus and nitrogen, are the most common non-point source pollutants.

Saskatchewan Environment (2006) describes stormwater as "rainfall and snowmelt that runs off the land into storm sewers, streams and nearby lakes or rivers." Stormwater is a non-point source pollution which collects contaminants such as oil, grease, fertilizers, pesticides, metals, and sediment as it flows over the land. The quality and management of stormwater is not specifically regulated in Saskatchewan, however, *The Environmental Management and Protection Act (EMPA)* allows for regulations of stormwater to be created.

The quantity and quality of stormwater vary temporally and geographically (Chambers et al. 2001). Urban stormwater can affect the hydraulic characteristics, stream morphology, aquatic habit, and public health and recreation of receiving surface waters (U.S. EPA 1999). These impacts can be short-term due to storm events or long-term due to cumulative effects of repeated stormwater discharges from multiple sources (Saskatchewan Environment 2006b).

2.3.1 Phosphorus in Urban Stormwater

Phosphorus is one of the primary nutrients of concern in stormwater originating mainly from urban landscape runoff such as fertilizers, detergents, plant debris, and animal waste (Saskatchewan Environment 2006b; U.S. EPA 1999). Approximately 95% of P in stormwater is in particulate form compared to 65 to 100% being bioavailable in wastewater (Chambers et al. 2001). The majority of soluble phosphorus in urban stormwater is in the form orthophosphate. The quality of stormwater is influenced by land use (Table 2.12). Typical stormwater qualities in the prairies are shown in Table 2.13.

Table 2.12 Median event mean concentrations for urban land uses (adapted from U.S. EPA 1983b)

Pollutant	Units	Predominantly Residential	Mixed Residential/ Commercial	Predominantly Commercial	Open/Non-Urban
TSS	mg/L	101	67	69	70
Total P	µg/L	383	263	201	121
Soluble P	µg/L	143	56	80	26
TKN	µg/L	1900	1288	1179	965
Nitrate + Nitrite	µg/L	736	558	572	543
BOD	mg/L	10	7.8	9.3	-
COD	mg/L	73	65	57	40

Table 2.13 Typical stormwater quality for selected pollutants. Means are in parenthesis (adapted from Saskatchewan Environment 2006b)

Pollutant (mg/L)	SK Community A (2003)	SK Community B (2005)	Edmonton	
			Spring	Summer
TSS	52 – 139 (88)	129 – 324 (268)	155 – 290 (223)	104 – 227 (166)
Total P	0.18 – 0.41 (0.36)	0.95 – 1.08 (1.03)	0.88 – 1.08 (0.98)	0.42 – 0.69 (0.56)
TDP	-	-	0.4 – 0.54 (0.47)	-
TKN	0.8 – 4 (2.1)	2.3 – 4.1 (3.2)	4 – 5.2 (4.6)	0.9 – 2.3 (1.6)
NO_3^--N	< 0.02 – 2.07 (0.84)	0.42 – 1.48 (0.85)	-	-
NH_3-N	-	-	1.14 – 1.6 (1.37)	0.48 – 0.67 (0.58)
Total N	-	-	5.9 – 6.2 (6.1)	4.2

2.3.2 Phosphorus Removal in Stormwater Ponds

A common and cost effective stormwater best management practice is retention ponds (Figure 2.7). Retention ponds are designed to capture and store a specific volume of runoff. The water is retained until it is displaced by another storm event. The water is treated for pollutants by sedimentation and the biological and biochemical mechanisms of aquatic plants and microorganisms. Due to the permanent pool of water settled sediments are not likely to re-suspend and wash out.

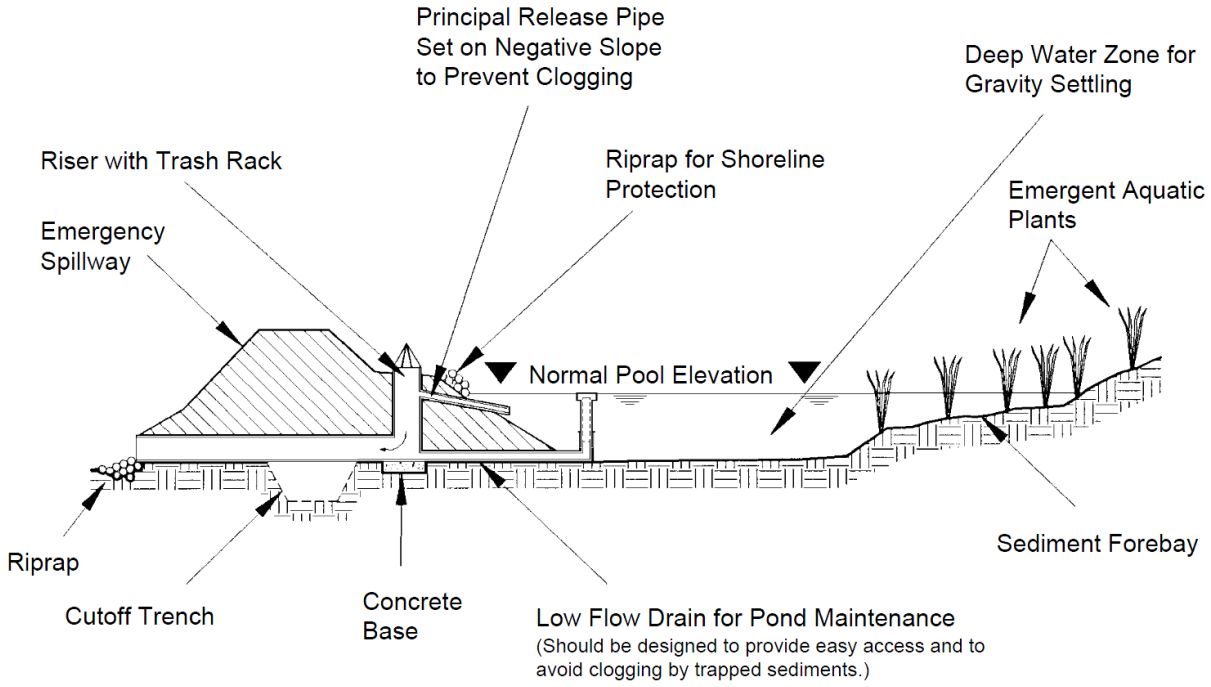

Figure 2.7 Profile of a typical wet pond (NVPDC AND ESI 1992)

Phosphorus removal in retention ponds occurs by sedimentation of phosphorus associated with suspended solids and by uptake from algae and microorganisms. The average total phosphorus removal is approximately 52% ± 23% (67% confidence interval) (Weiss et al. 2007). The phosphorus concentration of settled sediments for 23 stormwater ponds ranged from 110 to 1938 mg/kg with an average of 583 mg/kg (Schueler and Yousef 1994).

2.4 Agricultural Runoff

Agriculture is an important industry that occupies substantial landmass. Approximately 7% of Canada's total land area is agricultural land (Chambers et al. 2001). The impact of nutrient losses from agricultural on water quality is a concern for many nations (Chambers et al. 2001) The largest contribution of non-point source pollution in the United States is agriculture (Zaimes and Schultz 2002). The major activities that contribute to pollution are cultivation, fertilizer and pesticide application, irrigation, planting, harvesting, confined animal facilities, and grazing (Zaimes and Schultz 2002).

2.4.1 Phosphorus in Agricultural Runoff

Phosphorus from agricultural runoff may contribute a greater proportion to inputs to surface water than point sources (Zaimes and Schultz 2002). There are no national estimates available of the quantity of P lost to surface waters from agricultural lands in Canada (Chambers et al. 2001). The agriculture share of non-point source P inputs to surface waters was 84% in the United States in 1998 and as high as 90% in New Zealand in 2000 (Zaimes and Schultz 2002). Approximately 31 and 17% of P discharged annually to surface waters in the United States was from cropland and pasture and rangeland respectively (Chambers et al. 2001). P is typically in particulate form when lost from agricultural lands (Zaimes and Schultz 2002; Chambers et al. 2001). Typical P concentrations of surface water impacted by agricultural practices are shown in Table 2.14.

Table 2.14 Phosphorus concentrations in stream and drainage water under various flow regimes. Ranges are in parenthesis when available (from Zaimes and Schultz 2002)

Flow Regimes	TP (unfiltered)	TP (<0.45)	Land Use
	mg/L		
Stormflow	1.5	1.0	Pasture with dairy operation, stream water
		0.15	Grassland, tile drains
	0.49 (0.14–2.37)		Pasture, stream water
	1.20 (0.16–4.30)		Riparian pine afforested 1, stream water
	1.43 (0.50–5.21)		Riparian pine afforested 2, stream water
	0.46 (0.07–3.30)	0.13 (<0.01–0.36)	Cropland (91%), stream water
Snowmelt	0.27 (0.09–0.90)	0.155 (0.02–0.45)	Cropland (91%)
Baseflow	0.8	0.4	Pasture with dairy operations, stream water
		0.050	Grassland, tile drains
	0.18 (0.07–0.60)		Pasture, stream water
	0.20 (0.06–0.47)		Riparian pine afforested 1, stream water
	0.32 (0.14–1.16)		Riparian pine afforested 2, stream water
	0.071 (0.02–0.61)	0.031 (<0.01–0.23)	Cropland (91%), stream water

2.5 Water Treatment Residual Solids

In order to characterize water treatment residual solids (WTRS) four important areas need to be addressed (Cornwell 2006):

1. Type of residual generated;
2. Quantity of residual generated;
3. Classification by physical properties and dewatering characteristics; and
4. Specific constituents in the residual streams, particularly as they may relate to proper disposal or beneficial use.

These factors will be influenced by geographical location, seasonal variations, source water, treatment design, and governing regulations.

2.5.1 Formation of WTRS

Typical surface water treatment plant processes involve coagulation, flocculation, sedimentation, and filtration to remove suspended solids from raw water. Treatment plants may also use lime softening to reduce the hardness of the water. The solid residuals generated from the treatment processes are composed of different compounds collected from the various stages of treatment. The residual solids are typically composed of minerals and humic material precipitated from raw water as well as solids from coagulation/sedimentation/filtration in the form of settled coarse solids from pre-sedimentation chambers, finer settled solids from the bottom of clarifiers after coagulation and softening, and very fine residual solids from filter backwash waters (Viessman et al. 2009). In conventional systems, filter backwash water and clarifier solid residuals are a significant portion of waste generated (Walsh et al. 2008).

2.5.2 Chemistry of WTRS

Common inorganic coagulants used are aluminum sulphate (alum), ferric sulphate, and ferric chloride as well as coagulant aids which are mostly organic polymers (Viessman et al. 2009). Aluminum (Al) and iron (Fe) hydroxides as well as calcium carbonate ($CaCO_3$), if lime softening is utilized, are typical precipitates from the coagulation process (Viessman et al. 2009; Elliott and Dempsey 1991). Sotero-Santos et al. (2005) sampled WTRS during a wet and dry season and found they differed in turbidity, suspended solids, nutrients, contents of metal (especially Al and Fe) and chemical oxygen demand (COD). In general, the elemental constituents may be similar among different WTRS, however, the quantity and quality are specific to each WTRS which are influenced by the source water quality and treatment design.

2.5.3 Other Pollutants of WTRS

WTRS will also contain pollutants from chemical impurities, disinfection by-products, and other materials from the source water that are concentrated when removed from drinking water. Several metals, such as arsenic, aluminum, and iron, could be present from the coagulants, their impurities, and from the source water. Coagulants produce precipitates in the form of inorganic insoluble hydrated metal oxides. Disinfection may form by-products, such as bromate and trihalomethanes, when disinfectants react with substances in the source water such as bromide and natural organic matter. Pollutants from the source water may comprise suspended and dissolved solids. Suspended solids include inorganic (silt, sand, and clay) and organic matter. Other pollutants in residuals can include nitrogen, pH, phosphorus, and radionuclides (U.S EPA 2011).

2.5.4 Management of WTRS

There are no formal federal regulations in Canada specific to the treatment and handling of residual streams from water treatment plants (Walsh et al. 2008). However, provinces have imposed regulations to control the direct discharge of untreated residual streams into surface water (Walsh et al. 2008). Substances discharged into the environment that may cause, is

causing, or has caused an adverse effect on the environment must be reported to Saskatchewan Environment as required by *The Environmental Management and Protection Act 2002.*

Saskatchewan has objectives and guidelines for effluent discharges as well as surface water quality objectives to maintain a standard of water quality for the protection of human and aquatic life (Saskatchewan Environment 2006a). Due to stricter regulations many water treatment plants opt for a residual management facility to treat residual streams. However, these facilities produce a concentrated solid waste that needs to be disposed. Many water treatment plants in North America have solid waste management practices where the solid residuals are dewatered and then disposed of in a landfill. However, there are associated costs that are incurred and the storage space required for the waste limits the sustainable lifespan of the landfill. In addition, as drinking water standards evolve, treatment technology will advance to be able to remove greater concentrations of contaminants. This will lead to increased contaminant concentration in the residual waste which could pose environmental risk from leaching at the landfill or could lead to the waste being categorized as hazardous if certain concentrations of contaminants exceed acceptable non-hazardous limits. Hazardous contaminants include arsenic, which is limited to 0.01 mg/L in drinking waters (Health Canada 2010), and radioactive material (Saskatchewan Ministry of Environment 2010). Considerations should be given to possible practical uses of the solid residuals which would otherwise be waste.

2.5.5 Recycling and Reuse of WTRS

There have been studies on the recycling and reuse of WTRS which fit into four main categories: use as building and construction materials, reuse in wastewater treatment processes, land-based applications, and miscellaneous (Babatunde and Zhao 2007). Studies concerned with uses of residual solids as building and construction materials look at brick making, manufacturing of cement and cementitious materials, and use in pavement and geotechnical works. Unfortunately, even when the final product could conform to industry standards, in order to justify their use, the chemical composition and the water and organic content of sludge products needs to be less variable and be more reliable (Babatunde and Zhao 2007).

The use of WTRS has shown to be beneficial in enhancing treatment performance in wastewater treatment processes (Babatunde and Zhao 2007). Wastewater treatment uses include coagulant recovery and reuse (Bustamante and Waite 1995), as coagulant in wastewater treatment (Guan et al. 2005), adsorbent for pollutants and metals in wastewater, co-conditioning and dewatering with sewage sludge (Lai and Liu 2004), and as constructed wetlands substrate (Leader et al. 2005).

Land-based application appears to be a sustainable method of WTRS disposal which include uses for structural soil improvement (Elliott and Dempsey 1991), for nutrient reduction in laden soils and runoff (Dayton and Basta 2005b), and as soil buffer (Elliott and Dempsey 1991). Other possible uses include landfill capping. Recycling and reuse of WTRS has many potential advantageous applications and is a sustainable alternative compared to disposal.

2.6 Adsorbent of Phosphorus

A characteristic of WTRS is their ability to adsorb phosphorus from solution which is due to the amorphous iron and aluminum hydroxide precipitates (Razali et al. 2007; Makris et al. 2005a,b; Galarneau and Gehr 1997). The crystallinity of the Al and Fe hydroxides influences the P adsorption capabilities of WTRS (Elliott et al. 2002) Adsorption of P also occurs by calcium carbonate ($CaCO_3$), although not as well as Al or Fe, and can remove P by calcium (Ca) phosphorus compound precipitates (Ippolito et al. 2003). Adsorption is the predominant removal mechanism for P removal with WTRS rather than precipitation or a water column aqueous reaction. The adsorption of P to the WTRS surfaces is an alternative to chemical precipitation or biological uptake. There have been many studies to determine the amorphous iron and aluminum hydroxide content and the maximum phosphorus adsorption capacity (Q_{max}) of WTRS (Babatunde and Zhao 2010; Gibbons 2009; Razali et al. 2007; Yang et al. 2006a; Dayton and Basta 2005a; Ippolito et al. 2003; Galarneau and Gehr 1997). However, there is a lack of Fe-based WTRS studies since most focus on Al-based WTRS.

2.6.1 Adsorption Theory

Adsorption is the adhesion of molecules of gas, liquid, or dissolved solids to a surface (Brownfields and Land Revitalization Technology Support Center 2012). The material being accumulated at the interface is the adsorbate and the material that adsorbs is the adsorbent. Interfaces can occur between combinations of solid, liquid, and gas phases. The understanding of the solid/liquid interface is less developed compared to the solid/gas interface, however, theoretically, solid/liquid interface interactions are similar to solid/gas interface interactions (Luth 1993). Therefore, description of the adsorption process at the solid/gas interface is generally applied for solid/liquid interfaces as well (Luth 1993). Adsorption is conventionally categorized as physisorption (weak interaction) or chemisorption (strong interaction) based on the strength of the interaction between the adsorbate and adsorbent (Oura et al. 2003; Luth 1993). It is difficult to differentiate between the two as the distinction is imprecise (Oura et al. 2003). The adsorption process involves three steps: macrotransport, microtransport, and sorption.

Equilibrium adsorption isotherms describe the separation of solute from solution onto an adsorbent and are useful for optimizing adsorbent use (Kundu and Gupta 2006). Phosphorus adsorption equilibrium is reached when the rate of P adsorption and desorption are equal (Crini and Peindy 2006). There are several isotherm equations available to describe equilibrium characteristics of adsorption. The single-component Langmuir and Freundlich isotherms are the most popular two-parameter isotherm equations (LeVan and Vermeulen 1981). Adsorption from solution is typically represented by the Langmuir, Freundlich, and Temkin equations (Xiong 2009). The Langmuir, Freundlich, and Temkin isotherm models are presented in detail below. The Brunauer-Emmett-Teller (BET), Dubinin-Radushkevich, Frumkin, and Harkins-Jura are described in Appendix A.

2.6.1.1 Langmuir Isotherm

The Langmuir isotherm is a widely used isotherm that is frequently used to represent adsorption from solution. The Langmuir adsorption isotherm model is based on three assumptions (Oura et al. 2003; Luth 1993):

1. Adsorption is limited by monolayer coverage;
2. All adsorption sites are equivalent; and
3. Only one molecule can reside on an adsorption site.

The first assumption is suitable for gases and acceptable for liquids (Droste 1997). The Langmuir isotherm is more applicable for chemisorption (Lowell et al. 2004).

The Langmuir isotherm is defined by the equation (Babatunde and Zhao 2010):

$$Q = \frac{Q_{max} k C_e}{1 + k C_e} \qquad [2.11]$$

where Q is the adsorption density (mg P g^{-1}), C_e is the equilibrium concentration in the liquid phase (mg P L^{-1}), Q_{max} is the theoretical maximum adsorption density (mg P g^{-1}), and k (L mg^{-1}) represents the affinity of the adsorbent for the adsorbate.

The linearized form of the Langmuir equation is presented by:

$$\frac{C_e}{Q} = \frac{1}{Q_{max}} C_e + \frac{1}{k Q_{max}} \qquad [2.12]$$

in the form y = mx + b, where a plot of C_e (x) vs. C_e/Q (y) gives the values for k and Q_{max}. Q_{max} is determined from the slope of the line ($1/Q_{max}$) and k from the y-intercept ($1/kQ_{max}$).

2.6.1.2 Freundlich Isotherm

The Freundlich isotherm is often used for heterogeneous surface energy systems (Xiong 2009). It has an exponential expression because it assumes that as the adsorbate concentration in solution increases so too does the concentration of adsorbate on the adsorbent surface (Kundu and Gupta 2006). The Freundlich isotherm is an empirical representation of experimental data (LeVan and Vermeulen 1981) and defined by (Babatunde and Zhao 2010):

$$Q = K_F C_e^{1/n} \qquad [2.13]$$

where Q is the adsorption density (mg P g^{-1}), C_e is the equilibrium concentration in the liquid phase (mg P L^{-1}), and K_F (L g^{-1}) and n are the Freundlich constants which represent the adsorption capacity and the adsorption intensity, respectively (Kundu and Gupta 2006).

The linearized form of the Freundlich equation is presented by:

$$\log Q = \frac{1}{n} \log C_e + \log K_F \qquad [2.14]$$

in the form y = mx + b, where a plot of log C_e (x) versus log Q (y) gives the values for K_F and n.

K_F is related to the bonding energy and 1/n is the heterogeneity factor in which n is a measure of the deviation from linearity of the adsorption (Zhao et al. 2007). When n is equal to unity then adsorption is linear, below unity the adsorption process is chemical, and above unity adsorption is a favourable physical process (Kundu and Gupta 2006).

2.6.1.3 Temkin Isotherm

The Temkin isotherm considers heterogeneous surfaces where no molecular interactions exist (Bockris and Reddy 1998). It assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions (Kundu and Gupta 2006). It assumes that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy (Kundu and Gupta 2006).

The Temkin isotherm is defined by (Babatunde and Zhao 2010):

$$Q = \frac{RT}{b} \ln(k_T C_e) \qquad [2.15]$$

where C_e is the equilibrium concentration in the liquid phase (mg P L^{-1}), R is the gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K), b is the variation of adsorption energy (J mol^{-1}), and k_T is the equilibrium binding constant (L mg^{-1}) corresponding to the maximum binding energy.

The linearized form of the Temkin equation is presented by:

$$Q = B_1 \ln k_T + B_1 \ln C_e \qquad [2.16]$$

where B_1 is equal to RT/b. A plot of ln C_e (x) versus Q (y) gives the values for the constants B_1, b, and k_T.

B_1 is related to the heat of adsorption, b is the variation of adsorption energy, and k_T is the equilibrium binding constant corresponding to the maximum binding energy (Kundu and Gupta 2006).

2.6.1.4 Isotherm Modelling of WTRS

Batch adsorption testing is typically performed using phosphate-spiked deionized water as a P source. Testing in P-spiked deionized water provides a bulk indication of the WTRS adsorption characteristics. Testing with phosphate-spiked deionized water allows for a consistent comparison of P adsorption capacity and isotherm development between adsorbents. Other sources of P, such as wastewater, may have competitive species and have inconsistent and unpredictable properties.

Dayton et al. (2003) performed batch adsorption tests with 21 Al-based WTRS and found that the P sorption isotherm data conformed well to the linearized Langmuir ($p < 0.05$) and the non-linear Freundlich ($p < 0.05$).

Zhao et al. (2007) modelled adsorption behaviour of an Al-based WTRS with Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms. Based on the R^2 and the error analysis using four different error functions Zhao et al. (2007) reported the Freundlich isotherm appeared to be the best for modelling adsorption behaviour of WTRS. The Langmuir and Temkin isotherms were also good models while the Dubinin-Radushkevich isotherms seemed inappropriate to describe the adsorption behaviour.

Babatunde and Zhao (2010) performed batch adsorption tests with an Al-based WTRS and fit the experimental data to Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Frumkin, and Harkins-Jura adsorption isotherm models. The Langmuir isotherm modelled adsorption behaviour of WTRS the best (R^2 = 0.97-0.98). Freundlich, Dubinin-Radushkevich, Temkin, and Frumkin isotherms were also acceptable models with R^2 ranging from 0.81 to 0.97. The Harkins-Jura isotherm model appeared to be a poor fit with an R^2 of 0.61-0.69.

Mortula and Gagnon (2007a) found that Langmuir isotherms did not effectively predict adsorption densities of oven dried alum WTRS in secondary municipal effluent. They found that the Freundlich isotherm parameters for adsorption in wastewater were comparable to Freundlich isotherm values found in P-spiked deionized water. Mortula and Gagnon (2007b) also found that

Langmuir isotherms were not effective for oven dried alum WTRS and aquaculture processing water and that Freundlich isotherm parameters were higher in aquaculture processing water than those found in deionized water.

Several other P adsorption studies have successfully used the Langmuir isotherm to model the adsorption behaviour of WTRS (Gibbons 2009; Razali et al. 2007; Dayton and Basta 2005a,b; Kim et al. 2003).

2.6.2 Maximum Phosphorus Adsorption Capacity

The Langmuir isotherm model has been shown to be a suitable model of the P adsorption behaviour of WTRS and allows for the maximum phosphorus adsorption capacity, Q_{max}, to be determined. Although there is no standardized batch adsorption procedure for creating isotherms (i.e. varying pH, WTRS particle sizes, and P concentrations) the P source used is typically a deionized phosphate-spiked solution. This allows for consistent Q_{max} determinations for a P adsorbent without competitive species compared to testing in wastewater with inconsistent and unpredictable properties.

Razali et al. (2007) performed batch adsorption tests at pH 4.0 with dewatered air dried alum sludge with particle size < 2.36 mm and obtained maximum adsorption capacities (Q_{max}) of 3.33, 2.41, and 1.57 mg P/g WTRS for orthophosphate, polyphosphate, and organic phosphate. Maximum adsorption capacities of 0.7-3.5 mg P/g WTRS were achieved for pH ranging from 9.0 to 4.3 using air dried alum residual solids (Yang et al. 2006a). Gibbons (2009) performed batch adsorption tests for 12 days at pH 6.2 on two alum, one lime, and one iron residual solids samples with particle sizes of < 250 µm and 425 µm. The Q_{max} of the two alum WTRS (425 µm) were 1.03 and 1.11 mg P/g WTRS, 1.39 mg P/g WTRS for the lime WTRS (< 250 µm), and 2.96 mg P/ g WTRS for the iron WTRS (425 µm). Babatunde and Zhao (2010) obtained Q_{max} of 10.2-31.9 mg P/g WTRS for pH ranging from 9 to 4 using air dried alum residual solids and a contact time of 48 hours. It appears that Al is a better adsorbent of P (Makris et al. 2005a; Elliott et al. 2002; Evans and Smillie 1976) although there have been cases where Fe performs better (Gibbons 2009).

The Q_{max} varies among residual solids as shown by a study in which Q_{max} ranged from 1.84 to 29.5 g P/kg solids for samples from 18 water treatment plants (Dayton and Basta 2005a). This is likely due to the different source water and chemical treatment processes at each location. However, Dayton and Basta (2005a) also showed that the testing procedure used, such as particle size, equilibrium time, and initial P concentration, yields significantly different P_{max} results. This trend of varying Q_{max} can be seen throughout the literature and comparative examples are summarized in Table 2.15.

Table 2.15 Comparison of maximum adsorption capacities of orthophosphorus of WTRS of various studies (adapted from Razali et al. 2007)

Test Conditions (Al-based WTRS unless specified)	Maximum Adsorption Capacity Q_{max} (mg P/g WTRS)	Reference
Initial P concentration 30.6-107.2 mg PO_4^{3-}/L Equilibrium time 72 h	150 (particle size < 0.5 mm) 73 (particle size > 4.0 mm)	Novak and Watts 2005
Particle size < 2.36 mm Initial P concentration 14.7 mg PO_4^{3-}/L pH 4.0 Equilibrium time 1 day	3.33	Razali et al. 2007
Particle size < 2 mm Initial P concentration up to 4000 mg PO_4^{3-}/L pH 7.1 Equilibrium time overnight	8.16	Kim et al. 2003
Particle size 0.063-2.36 mm Initial P concentration 15.3 mg PO_4^{3-}/L pH 4.3	3.5	Yang et al. 2006b
Not specified	0.097-0.11	Huang and Chiswell 2000
Particle size 0.1-0.3 mm Initial P concentration 918 mg PO_4^{3-}/L Equilibrium time 1 day	12.5	Ippolito et al. 2003
Particle size <2 mm Initial P concentration 0-306.5 g PO_4^{3-}/L Equilibrium time 17 h	0.3-5.14	Dayton et al. 2003

Table 2.15 continued

Test Conditions (Al-based WTRS unless specified)	Maximum Adsorption Capacity Q_{max} (mg P/g WTRS)	Reference
Particle size < 150 µm Initial p concentration 0-10.7 g PO_4^{3-}/L	1.84-29.5 (Equilibrium time 17 h) 10.4-37.0 (Equilibrium time 6 days)	Dayton and Basta 2005a
Particle size < 2 mm Initial P loading 30.6 mg PO_4^{3-}/g sludge Equilibrium time 10 days	7.5-10 (Four kinds of alum sludge tested)	Makris et al. 2005a
Alum Initial P concentration 4.60-5.36 mg PO_4^{3-}/L Lime Initial P concentration 5.36 mg PO_4^{3-}/L Ferric Initial P concentration 28.1 mg PO_4^{3-}/L pH 6.2 Equilibrium time 12 days	1.03-1.11 (Two kinds of alum sludge tested, Particle size 425 µm) 1.39 (Particle size < 250 µm) 2.96 (Particle size 425 µm)	Gibbons 2009
Particle size < 2 mm Initial P concentration 0-1103 mg PO_4^{3-}/L Equilibrium time 2 days	31.9 (pH 4) 10.2 (pH 9)	Babatunde and Zhao 2010

2.6.2.1 WTRS Compared to Other Adsorbents

Residual solids from the water treatment process compare well to other traditional adsorbents. Mortula et al. (2007) performed batch adsorption tests with alum residuals dried various ways as well as with other low-cost media and granular activated carbon (Table 2.16). Langmuir isotherms were used to model the adsorption behaviour of the media and to determine Q_{max}. The air dried alum WTRS, bone char, and granular activated carbon did not fit the Langmuir isotherm. The oven dried alum WTRS had the highest Q_{max} at 0.674 mg P/g among the residuals that fit the Langmuir isotherm model.

Table 2.16 Coefficients of Langmuir adsorption isotherms for materials tested in P-spiked deionized water (adapted from Mortula et al. 2007)

Materials	R^2	Q_{max} (mg P/g)	k (L/g P)
Oven dried sludge	0.8971	0.674	2.345
Air dried sludge	0.0970	1.787	0.284
Freeze-thaw dried sludge	0.9515	0.300	8.273
Blast furnace slag	0.9019	0.593	1.145
Cement kiln dust	0.9986	0.469	6.968
Bone char	0.2966	-0.548	-0.810
Limestone	0.8363	-0.015	-0.293
Granular activated carbon	0.0153	-3.766	-0.059

The phosphorus adsorption capacities of WTRS have a large range but in general are similar to other P adsorbents (Table 2.17).

Table 2.17 Phosphorus adsorption capacity of several P adsorbents reported in the literature

Adsorbent	Maximum Adsorption Capacity Q_{max} (mg P/g solid)	Reference
Al-based WTRS*	0.097-150	Various studies (Table 2.14)
Fe-based WTRS*	2.96	Gibbons (2009)
Ca-based WTRS*	1.39	Gibbons (2009)
Activated alumina	17.5	Shin et al. 2004
Al_{10}SBA-15	26.7	Shin et al. 2004
Blast furnace slag	44.2	Sakadevan and Bavor 1998
Ferrihydrite	42.78	Borggaard et al. 2005
Ferrihydrite-modified diatomite	37.3	Xiong 2009
Fly ash	0.86	Drizo et al. 1999
Goethite	6.42, 16.4	Borggaard et al. 2005; Oh et al. 1999
Hematite	2.2	Oh et al. 1999
Iron-hydroxide eggshell	4.73	Mezenner et al. 2009
Limestone	0.68	Drizo et al. 1999
Red mud with HCl treatment	0.58	Huang et al. 2008
Sand	0.129	Arias et al. 2001
Steel slag	5.3	Xiong et al. 2008
Synthesized aluminum oxide	35.03	Borggaard et al. 2005
Synthesized iron oxide coated sand	0.49	Boujelben et al. 2008
Zeolite	0.46, 2.15	Drizo et al. 1999; Sakadevan and Bavor 1998

* Varying pH, particle sizes, and other testing conditions

2.6.3 Testing Conditions for Maximum Phosphorus Adsorption Capacity Determination

There are no standard testing conditions for determining the adsorption capacities of WTRS. The testing conditions can affect the results for Q_{max} of WTRS as shown by the wide spectrum of results reported in the literature. Conditions such as pH, P form, initial P concentration, and particle size have an effect on the maximum adsorption capacity.

2.6.3.1 pH

Razali et al. (2007) performed batch adsorption tests with dewatered alum WTRS. The adsorption was highly dependent on pH performing the best at low pH. Zhao et al. (2007) observed the same trend of higher Q_{max} at lower pH.

Mortula (2006) performed batch adsorption experiments with oven dried alum sludge and orthophosphate-spiked deionized water of various pH and found that pH had little effect on the adsorption density. For the test conditions utilized he found that removals of P for all pHs were above 50% with most being more than 90% and that a pH of 5 appeared to produce maximum adsorption density.

The pH significantly impacted the adsorption capacity of air dried alum WTRS (Yang et al. 2006a). The adsorption capacity was at a maximum of 3.5 mg P/g sludge at pH 4.3 and decreased to 0.7 mg P/g sludge at pH 9. Yang et al. (2006a) reported this may be due to OH^- competing with phosphate for adsorption sites as pH increases.

2.6.3.2 Phosphorus Form

Adsorption capacities are dependent upon the P form in the order of orthophosphate > polyphosphate > organic phosphate (Babatunde and Zhao 2010; Razali et al. 2007; Zhao et al. 2007; Kim et al. 2003; Galarneau and Gehr 1997). These studies (except Galarneau and Gehr 1997) investigated P adsorption with air-dried alum WTRS in batch tests using various P forms spiked in aqueous solutions. The residuals were crushed and sieved with equilibrium test times

ranging from 17 hours to 80 days. Galarneau and Gehr (1997) performed batched sorption tests using pure aluminum hydroxide and an equilibrium time of 60 minutes. However, the studies all consistently found the phosphorus forms were adsorbed in the order of orthophosphate > polyphosphate > organic phosphate.

2.6.3.3 Initial P Concentration

Mortula (2006) performed batch adsorption experiments with oven dried alum sludge and orthophosphate-spiked deionized water of various initial P concentrations. It appeared that high initial P concentration would generate consistently higher adsorption density however, the oven dried alum sludge overall was effective in removing P from various concentrations.

2.6.3.4 Particle Size

Dayton and Basta (2005a) performed batch adsorption tests with 18 air dried alum WTRS. The Q_{max} ranged from 0.66 to 16.5 g P/kg sludge with a mean of 3.93 g P/ kg sludge for a particle size of < 2 mm. When the particle size was changed to < 150 µm the Q_{max} ranged from 1.84 to 29.5 g P/kg sludge which is a mean increase of 2.46-fold. Mortula (2006) performed batch adsorption experiments with oven dried alum sludge of various particle sizes and orthophosphate-spiked deionized water. Fine particles resulted in higher adsorption density than coarse particle sizes. This is likely due to fine particles having more surface area for adsorption. Zhao et al. (2007) performed batch adsorption tests with fine (0.06-0.13 mm) and coarse (0.35-0.45 mm) alum WTRS and found that the Q_{max} of fine particles was approximately 2 to 5 times as much as that of coarse particles. Novak and Watts (2005) reported Q_{max} of 150 mg P/g WTRS for fine-sized particles (< 0.5 mm) and 73 mg P/g WTRS for coarse-sized particles (> 4 mm). They also found that the equilibrium time was longer for coarser particles than for finer.

2.6.4 Aging of WTRS

Yang et al. (2008) studied the aging effects of Al-based WTRS over an 18 month period and determined that aging had no significant effects regarding the max adsorption capacity, the amorphous structure, surface area, pore area, and pore size distribution.

After a period of 242 days, alum that was applied to two southern California lakes underwent went chemical and mineralogical changes as it went from amorphous to crystalline structure and a loss of surface area (Berkowitz et al. 2005).

Alum floc aged for 6 months had a decreased maximum adsorption capacity, an increase in crystallinity, and decreased surface area (Berkowitz et al. 2006). The maximum adsorption capacity of aged alum floc was about 50% lower than freshly precipitated floc.

Incubation of Al-based WTRS with no P at 70°C resulted in changes in crystallinity as well as significant decreases (within the first month of a 24 month incubation) in specific surface area (SSA) and micropore volume with time (Makris et al. 2005b). However, Al-based WTRS treated with P had smaller changes in SSA values and remained amorphous for the 24 month 70°C incubation. Untreated Fe-based WTRS resulted in less drastic changes when incubated at 70°C for 24 months. Untreated and treated Fe-based WTRS also remained amorphous for the duration of incubation. It appears that P impedes the crystallization of WTRS.

de Vicente et al. (2008) found that $Al(OH)_3$ aged in solution with PO_4^{3-} maintained the adsorption capacity through 6 months but when aged without PO_4^{3-} present it lost 75% of the maximum adsorption capacity within 90 days. However, $Al(OH)_3$ aged in absence of PO_4^{3-} desorbs PO_4^{3-} more easily (99% recovered after 3 months) compared to $Al(OH)_3$ aged in presence of PO_4^{3-} (14% recovered after 3 months).

2.6.5 Desorption of Phosphorus

It has been shown that desorption of P from P loaded water treatment residual solids decreased with increasing desorption time (Makris et al. 2005a; Ippolito et al. 2003) and is minimal (Dayton and Basta 2005a; Makris et al. 2005a; Makris et al. 2004). Lookman et al. (1995) found that P desorbability decreased with increasing Al_{ox} + Fe_{ox} content of 44 German and Belgian soils. The exposure of WTRS to elevated temperatures could reduce P desorption (Makris and Harris 2006).

Typically less than 0.2% of the total P adsorbed was desorbed off of Al-based WTRS after 10 to 20 days in a 5 mM oxalate solution (Makris et al. 2005a). P-loaded Al- and Fe-based WTRS were exposed to 5 mM oxalate solution for 1-80 days and desorbed 0.2% and 0.8% of sorbed P (Makris et al. 2004). P loaded Al-based WTRS were subjected to serial extractions with 0.1 M KCl daily for 6 days and retained 91 to 104% of the calculated final Q_{max} (Dayton and Basta 2005a).

Makris et al. (2005b) showed increased stability of P bound to Al and Fe hydroxides that were incubated at 70°C for 24 months suggesting that P sorbed may be stable for at least 2 years. Al-based WTRS added to manure-fertilized soils immobilized P and remained stable for 7.5 years suggesting WTRS-immobilized P will remain fixed indefinitely as long as the WTRS remain intact (Agyin-Birikorang et al. 2007).

2.6.6 Ammonium Oxalate-Extractable Al and Fe and Maximum Phosphorus Adsorption Capacity Relationship

Accurate Q_{max} estimates of WTRS are important for proper and effective applications of WTRS. A possible relationship exists between acid ammonium oxalate extractable Al and Fe and the max phosphorus adsorption of the WTRS (Dayton and Basta 2005b; Dayton et al. 2003; Elliot et al. 2002, Evans and Smillie 1976). The crystallinity of Al and Fe hydrous oxides directly impacts their ability to sorb P (Elliott et al. 2002). Non-crystalline oxides are often measured by oxalate

extraction (McKeague et al. 1971). Therefore, the P-sorbing capacity of WTRS should be related to the oxalate-extractable Al + Fe (Al_{ox} + Fe_{ox}).

Elliot et al. (2002) added WTRS (Al-, Fe-, and Ca-based) to sandy soil amended with biosolids and found that the WTRS P sorbing ability could be predicted by the (Al_{ox} + Fe_{ox}) content of the WTRS. Dayton et al. (2003) found a significant linear relationship ($R^2 = 0.66$, $p < 0.05$) between runoff P reduction and Al_{ox} and Q_{max} but not with Fe_{ox} when simulating runoff water over silt loam planted with Bermuda grass and treated with poultry litter and WTRS. Using 18 different Al-based WTRS Dayton and Basta (2005a) were able to find a significant relationship ($R^2 = 0.916$, $p < 0.001$) between Q_{max} and Al_{ox}. Adding Fe_{ox} (Al_{ox} + Fe_{ox}) did not improve the relationship. However, the testing conditions for determining Q_{max} and high amorphous metal oxide in WTRS mean that an accurate determination of Q_{max} and Al_{ox} is essential to create a predictive model and to use WTRS effectively. The relationship between Q_{max} and (Al_{ox} + Fe_{ox}) would be beneficial for Q_{max} predictions by eliminating excessive batch adsorption tests required to produce isotherm models.

2.6.7 Reuse of WTRS for Phosphorus Removal Treatment

2.6.7.1 Soil and Agricultural Applications

Studies of WTRS as a possible soil addition for control of P solubility and P release have been performed in soil sciences. The studies have tended to be concerned with P release from soils enriched with biosolids such as manure or secondary wastewater treatment plant sludge (Agyin-Birikorang et al. 2007; Dayton and Basta 2005b; Dayton et al. 2003; Elliott et al. 2002; Peters and Basta 1996).

Agyin-Birikorang et al. (2007) amended manure-impacted soils with Al-based WTRS and found that it reduced water-soluble P by ≥ 60% as well as total dissolved P and bioavailable P by > 50% from rainfall runoff and leachate from the soils. Twenty-one air dried Al-based WTRS were added to box plots of silt loam planted with Bermuda grass treated with poultry litter and reduced runoff P by 14.0-84.9% (Dayton et al. 2003). Dayton and Basta (2005b) used 5 air dried Al-

based WTRS to reduce P by (i) creating a buffer strip for surface runoff over Tonti silt loam and poultry litter, (ii) incorporating directly into the soil, and (iii) co-blending with poultry litter and biosolids. The maximum runoff dissolved reactive P reduction achieved by the buffer strip was 66.8 to 86.2% while the maximum $CaCl_2$-P reductions for the WTRS soil incorporation was 60.9 to 96.0% and > 75% for co-blending with biosolids.

Elliott et al. (2002) monitored leachate P from columns filled with Immokalee soil amended with biosolids or triple superphosphate (TSP). Without WTRS, 11% of biosolids amended total P and 21% of TSP amended total P leached over 4 months. The biosolid and WTRS treatment reduced P in leachate to a level that was not statistically different from the soil only control leachate. The TSP and WTRS treatment reduced leachate P to 3.5% (Fe-based), 2.5% (Ca-based), and < 1% (Al-based).

2.6.7.2 Wastewater Applications

Literature regarding the use of water treatment residual solids, especially in the form of slurry and not cake, for P control from municipal facilities is lacking. There have been studies done that investigate the potential use of WTRS for removal of P from secondary effluent and from aquaculture wastewaters (Gibbons 2009, Gibbons et al. 2009; Mortula and Gagnon 2007a,b,c; Mortula et al. 2007; Mortula 2006; Huang and Chiswell 2000). Many of these studies used column applications for P removal. Most of the studies achieved phosphorus removal greater than 90% with WTRS being a more effective adsorbent of orthophosphate than total phosphate phosphorus.

Gibbons (2009) performed batch adsorption experiments with oven dried alum, ferric, and lime WTRS and municipal wastewater effluent containing 4.2 mg P/L. The initial pH of the wastewater was 6.8 and not adjusted. The batch solutions were shaken at 200 rpm for 51 hours. The phosphate removal ranged from 93.7% to 96.6% for all WTRS.

Mortula et al. (2007) performed batch adsorption experiments with air, oven, and freeze-thaw dried alum WTRS and municipal wastewater effluent with an orthophosphate concentration of

approximately 5 mg/L. All types of dried alum sludge achieved > 80% removal of phosphorus with greater orthophosphate removal than total phosphorus. The pH of the wastewater after treatment was approximately 6.5 for all WTRS which would be acceptable for disposal of effluent into surface water.

Mortula (2006) performed batch adsorption experiments with air dried alum WTRS and secondary municipal effluent, pilot and bench scale biofiltration effluent, and aquaculture process water. The residuals removed approximately ≥ 85% of orthophosphate and ≥ 80% of total phosphorus from the secondary effluent. The pH of the raw wastewater was 7.23 and decreased with increasing WTRS dosage to 5.69-6.16. The WTRS were able to remove ≥ 70% of phosphorus from pilot and bench scale biofiltration effluent. The pH of the biofiltration effluent was approximately 6.55 and decreased with the addition of WTRS (as low as 5.31) but the decrease could not be correlated with the WTRS dosage. The WTRS achieved approximately ≥ 90% removal of orthophosphate and ≥ 60% of total phosphorus from aquaculture process water. The pH of the aquaculture process water was 7.75 and decreased with the addition of WTRS to 5.91-6.55. The alum WTRS were more effective at removing orthophosphates than total phosphorus for all wastewater types. Column tests were also performed with alum WTRS and the four wastewater types. Similar phosphorus removals were achieved with final effluent pH levels being acceptable for disposal to surface water.

2.6.8 Toxicity of WTRS

2.6.8.1 Aluminum Toxicity

Aluminum is an abundant and ubiquitous element in the environment that it is difficult to measure its toxicity. The majority of aluminum in the world has no measured toxic effect (Cornwell 2006) however soluble aluminum has shown to be toxic to a variety of plants and animals. Aluminum is amphoteric and its chemistry in water is essentially that of aluminum hydroxide. The hydrolysis reactions of aluminum in water are (Cornwell 2006):

$$Al(H_2O)^{3+}_6 + H_2O = Al(H_2O)_5OH^{2+} + H_3O^+ \quad [2.17]$$

$$Al(H_2O)_5OH^{2+} + H_2O = Al(H_2O)_4(OH)^+ + H_3O^+ \quad [2.18]$$

$$Al(H_2O)_4(OH)_2^+ + H_2O = Al(H_2O)_3(OH)_3 + H_3O^+ \quad [2.19]$$

$$Al(H_2O)_3(OH)_3 + H_2O = Al(H_2O)_2(OH)_4^- + H_3O^+ \quad [2.20]$$

The solubility of aluminum is important when determining its toxicity. The colloidal aluminum hydroxide present in water treatment sludge increases the solubility of aluminum. The crystallization of aluminum hydroxides decreases the solubility. The soluble aluminum concentrations of WTRS will differ between fresh and aged sludge. Aluminum can also react with other substances in the water such as inorganic ligands and natural organic materials. Reactions with aluminum can change the form of aluminum present and its solubility (Cornwell 2006).

Berkowitz et al. (2005) dosed water samples from two southern California lakes with alum and found that the water samples had a decrease in pH, alkalinity, and dissolved Si concentrations and increases in SO_4^{2-} concentrations. The pH levels returned to pre-treatment levels within 15-30 days after application. The dissolved Al levels increased over the first 30-50 days after treatment which was consistent with solubility equations for $Al(OH)_3$.

Desorption of Al was studied by Ippolito et al. (2003) by shaking P-loaded Al-based WTRS for 1 to 211 days in a 0.01 M $CaCl_2$ solution. The pH and the desorbed Al concentrations increased with increased shaking time. Between day 84 and 211 the aluminum concentration increased significantly which could be due to dissolution of amorphous $Al(OH)_3$ and formation of the solution species $Al(OH)_4^-$. The increase in Al concentration was expected since Al undergoes hydrolysis as pH increases.

Three main dominant vegetation types are affected by discharge from the Gaba II water treatment plant (Kaggwa et al. 2001). Samples were taken along a transect following the flow path through the vegetation. The water quality and sediment chemistry of a natural wetland on the shores of Lake Victoria at Gaba in Uganda were unaffected by the discharge of alum sludge. However, the discharge appeared to cause low productivity and the apparent phasing out of

Cyperus paprus L. which is the dominant macrophyte in the Gaba swamp. There were also root abnormalities present. The alum sludge resulted in P deficiencies in the plants.

Daphnids were exposed to alum and ferric sludges for acute (48 h) and chronic (14 day) periods to observe their toxicity effects (Soteros-Santos et al. 2005). Alum and ferric chloride sludges caused chronic toxicity to *Daphnia similis.* demonstrated by low reproduction and some mortality but did not cause acute toxicity. Alum sludge was less toxic than ferric chloride sludge however both may impair receiving waters.

Alum sludges from ten water treatment plants in North America had their toxicity effects observed on the alga *S. capricornutum*, marine bacterium, the protozoan *T. pyriformis*, and fathead minnow (George et al. 1995). The alga *S. capricornutum* was the most sensitive to alum WTRS. Extracts that were obtained with pH 5 receiving water inhibited algal growth but typically not at neutral conditions. If the receiving water had a hardness less than 35 mg $CaCO_3$/L then alum sludge extracts prepared with receiving water were toxic to *S. capricornutum* at all pHs. The aluminum concentrations of the WTRS appeared to not be proportional to their impact on the growth of *S. capricornutum*.

Al-based WTRS should have no negative impacts on the environment and biological systems when appropriate rates (based on the chemical characteristics of the WTRS) are land applied (Agyin-Birikoran et al. 2013; Mahdy et al. 2012).

2.6.8.2 Other Toxicity Issues

Mahdy et al. (2012) performed lysimeter tests with air dried WTRS collected in Egypt. The WTRS reduced plant metal accumulation and soil metal extractability demonstrating WTRS ability to immobilize metals in soils.

Agyin-Birikoran et al. (2013) found five Al- and Fe-based WTRS in Florida contained total barium, cadmium, chromium, copper, lead, zinc, sodium, and molybdenum at concentrations well below the Florida groundwater guidance concentration and residential soil cleanup target

level values. Pathogens are typically not a problem in air dried Al- and Fe-based WTRS (< 20 coliforms/g) due to air drying, long term storage, and chlorine addition during the drinking water purification process (Agyin-Birikoran et al, 2013).

2.7 Research Contribution

As noted in the previous sections there have been several studies of the chemical and physical characteristics of WTRS as well their P adsorption capabilities. Much of the research of WTRS application has focused on soil sciences and the improvement of soil phosphorus retention (Agyin-Birikorang et al. 2007; Dayton and Basta 2005b; Dayton et al. 2003; Elliott 2002; Peters and Basta 1996; Elliott and Dempsey 1991). There have also been many studies to determine the amorphous iron and aluminum hydroxide content and the maximum phosphorus adsorption capacity (Q_{max}) of WTRS (Babatunde and Zhao 2010; Gibbons 2009; Razali et al. 2007; Yang et al. 2006a; Dayton and Basta 2005a; Ippolito et al. 2003; Galarneau and Gehr 1997).

Wastewater treatment studies have been done that investigate the potential use of WTRS for removal of P from secondary effluent and from aquaculture wastewaters (Gibbons 2009; Gibbons et al. 2009; Mortula and Gagnon 2007a,b,c; Mortula et al. 2007; Mortula 2006; Huang and Chiswell 2000). Many of these studies used column applications for P removal. However, these previous wastewater treatment studies focus on WTRS that have been collected as cake from WTPs, then air or oven dried, and finally crushed and sieved to desired particle sizes.

This study contributes to WTRS research by conducting investigations of WTRS adsorption characteristics and their treatment application in non-dried slurry form collected from clarifiers directly. Phosphorus adsorption applications of the collected WTRS were investigated through batch treatment of primary wastewater effluent (a surrogate to lagoon wastewater) and agricultural runoff water.

CHAPTER 3 Methodology

3.1 Samples

3.1.1 Water Treatment Residual Solids

Aluminum and iron based water treatment residual solids (WTRS) samples were collected from the Saskatoon, Prince Albert, and Buffalo Pound Water Treatment Plants (WTP). The selection of WTRS offers diverse compositions. Samples were collected from the same location each plant at two times during the year in an effort to observe seasonal effects. The WTRS collected at the earlier time of the year will be referred to as Sample 1 (Summer) and the later collected WTRS will be referred to as Sample 2 (Fall). The samples were decanted and stored at 4°C. The Total Solids (TS) and Total Suspended Solids (TSS) of the decanted WTRS were determined, following methods 2540B and 2540D from Standard Methods for Examination of Water & Wastewater (APHA-AWWA-WEF 2005), in order to determine the mass concentration of the sludge for application. Testing and applications of WTRS were done with the WTRS in slurry form.

3.1.1.1 Saskatoon

The Saskatoon WTP draws and treats water from the South Saskatchewan River (City of Saskatoon 2012). The Saskatoon surface water treatment process is described below (City of Saskatoon 2012). Water is first moved through coarse screens and a grit sedimentation chamber followed by sand separators removing smaller particles of sand down to 400 microns (R. Munro, personal communication April 22, 2013). Potassium permanganate is added to reduce taste and odour. Ferric sulphate coagulant is added in clarifiers to cause flocculation and settle suspended solids. Lime is also added to soften the water resulting in the formation of insoluble carbonates and hydroxides that settle out. After clarification chlorine and sodium silico fluoride are added as water flows into a contact basin. Chlorine is used for disinfection while fluoride is added to help prevent tooth decay. The contact basin allows for increased settling as well as adequate disinfection time. Filtration is performed using sand and crushed anthracite filters. Ammonia

hydroxide is added after filtration to form chloramines which continue disinfection through the distribution system. The treated water is stored in a clear well and pumped into the distribution system. Saskatoon WTP has a residual solids management facility where residuals from the backwash water, filters, clarifiers, and chlorine contact basin are dewatered. The residuals are concentrated and filter pressed into a solid cake which is transported to the landfill.

The iron residual solids from the Saskatoon WTP were collected from a river outfall during a clarifier blowdown (Figure 3.1) on June 9 and November 4, 2011.

Figure 3.1 Saskatoon water treatment plant river outfall where WTRS were collected

3.1.1.2 Prince Albert

The Prince Albert WTP draws and treats water from the North Saskatchewan River (City of Prince Albert 2011). The Prince Albert surface water treatment process is described below (City

of Prince Albert 2011). A conventional coagulation/flocculation/sedimentation/filtration treatment process is utilized. Potassium permanganate is added as an oxidizer before the clarifier. The plant uses alum (aluminum sulphate) as a coagulant in the clarifier for flocculation. Lime is also added in the clarifier for hardness and pH control. When the WTRS were sampled, Prince Albert used a gravity system clarifier. This was upgraded in the fall of 2011 to a high rate ballast and sand clarification system where sand is used as the main method to remove solids. Ultraviolet light treatment was also installed to assist in disinfection in conjunction with chlorine.

The alum residual solids from the Prince Albert WTP were collected from a sampling drain during a clarifier blowdown (Figure 3.2) on July 20 and August 25, 2011.

Figure 3.2 Prince Albert sample drain where WTRS were collected

3.1.1.3 Buffalo Pound

The Buffalo Pound WTP draws and treats water from Buffalo Pound Lake in Saskatchewan (Buffalo Pound Water Administration Board 2011). The Buffalo Pound surface water treatment process is described below (Buffalo Pound Water Administration Board 2011). Chlorine is added to the water for disinfection. The water then flows over cascades to remove excess oxygen produced by algae. Alum (aluminum sulphate) is added in the clarifier for flocculation and settling of solids. Water is passed through mixed-media filters of coarse anthracite and finer sand to remove remaining particulate matter and floc. The water then passes through granular activated carbon (GAC) to remove dissolved organic impurities responsible for taste and odour. During the winter and spring the carbon is regenerated in a furnace while in the summer and fall it is treating water in the filters. The sludge from the clarifiers is sent to wastewater lagoons where it is dewatered by freeze/thaw cycles and then disposed of in a landfill.

Alum residual solids from the Buffalo Pound WTP were collected on July 27 and October 25, 2011 from a sump that contained clarifier residuals (Figure 3.3) prior to them being sent to wastewater lagoons.

Figure 3.3 Buffalo Pound water treatment plant sump where WTRS were collected

3.1.2 Wastewater Samples

Three wastewater samples were collected for P removal treatment with the WTRS. Primary effluent was collected on March 15, 2012 from the Saskatoon wastewater treatment plant as a surrogate for sewage lagoon wastewater. Urban stormwater runoff was collected from six stormwater retention ponds in Saskatoon between December 2011 and July 2012. Agricultural runoff water was collected on August 21, 2012 from a pond behind Saskatoon Livestock Sales which is located 10 km west of Saskatoon, Saskatchewan on Highway #14.

3.2 Chemical Characterization

3.2.1 Water Treatment Residual Solids

3.2.1.1 Aluminum and Iron

The Al, Fe, and Ca content of each WTRS were determined. Extraction of Al and Fe from the WTRS was done using a variation of the acid ammonium oxalate method (McKeague and Day 2008). The extraction was performed using a mixture of 100 mL of 0.2 M (28.3 g L^{-1}) ammonium oxalate solution [$(NH_4)_2C_2O_4 \cdot H_2O$] (Fisher Scientific) and 76 mL of 0.2 M (25.2 g L^{-1}) oxalic acid solution [$H_2C_2O_4 \cdot 2H_2O$] (May & Baker Laboratory Chemicals) adjusted to pH 3. Sludge was oven dried at 105°C for 1-3 days to evaporate the water. The WTRS were crushed to less than 2 mm and weighed to 0.5 g samples. The WTRS were put in a plastic centrifuge tube with 40 mL of the acid ammonium oxalate solution and shaken in the dark for 4 hours with a wrist action shaker. After shaking, the tubes were centrifuged for 20 minute at 510 *g* (gravitational acceleration). The supernatant was decanted and stored in a dark refrigerator until analysis of Al and Fe was conducted. Extracted Al and Fe were measured using atomic adsorption spectrophotometry (Model 5000, Perkin-Elmer, Inc., Waltham, MA), following methods 3111D and 3111B (APHA-AWWA-WEF 2005), within one week of extraction.

3.2.1.2 Calcium

Extraction of Ca from the WTRS was done using a variation of the ammonium acetate method (Lavkulich 1981). Sludge was oven dried at 105°C for 1-3 days to evaporate the water. WTRS were crushed to less than 2 mm and weighed to 1.5 g samples. These samples were added to plastic centrifuge tubes with 30 mL of 1 M (77.08 g L^{-1}) ammonium acetate solution [NH_4OAc] (Fisher Scientific). The tubes were shaken for 5 minutes with a wrist action shaker and then stood for 24 hours. After 24 hours, the tubes were shaken with a wrist action shaker for 15 minutes. The contents of the tubes were filtered through 0.45 µm mixed cellulose ester (MCE) filters (Fisher Scientific). The leachate was then transferred to 200 mL volumetric flasks and made up to volume with 1 M NH_4OAc. The solutions were mixed and then stored in a

refrigerator until analysis of Ca was conducted. Extracted Ca was measured using atomic adsorption spectrophotometry (Model 5000, Perkin-Elmer, Inc., Waltham, MA), following method 3111B (APHA-AWWA-WEF 2005) within one day of extraction.

3.2.1.3 pH

The pH of the WTRS was determined using the method outlined by Hendershot et al. (2008). Sludge was oven dried for 1-3 days to evaporate water. The dried WTRS were crushed to < 2 mm. WTRS samples were weighed to 10 g and added to a beaker with 20 mL of deionized water. The solution was mixed intermittently for 30 minutes then stood for 1 hour. The pH of the supernatant was then measured with a pH probe (827 pH Lab, Metrohm, Switzerland).

3.2.2 Wastewater Samples

The pH of the wastewater samples was found using a pH probe (827 pH Lab, Metrohm, Switzerland). Unfiltered and filtered orthophosphate and total phosphorus were measured. Filtered wastewater samples were filtered through 0.45 µm MCE filters (Fisher Scientific). Orthophosphate was measured using the stannous chloride method [Method 4500-P D] (APHA-AWWA-WEF 2005) and a spectrophotometer (DR-4000, Hach Co., Loveland, CO). Total phosphorus was measured using the persulphate digestion and stannous chloride methods [4500-P B and 4500-P D] (APHA-AWWA-WEF 2005) and a spectrophotometer (DR-4000, Hach, Co., Loveland, CO).

3.3 Phosphorus Adsorption

3.3.1 Preliminary Time to Equilibrium Test

The duration of the isotherm test was set as the elapsed time until equilibrium when P was approximately no longer being removed from the solution by WTRS. The time to equilibrium was determined by using jar test apparatus to continuously mix suspensions containing identical initial P concentration and identical WTRS dosages. However, the WTRS dosage varied between

the three residual sources. One jar per day was removed and the remaining P concentration measured until the remaining concentration was constant. Testing was performed at room temperature and there was no pH adjustment.

A stock solution of 10 g P/L was made by adding 21.9 g of potassium phosphate [KH_2PO_4] (EM Science) to 500 mL of deionized water. The initial concentration of the jars was approximately 2 mg P/L by adding 0.2 mL of the P stock solution to 1000 mL of deionized water. The dosages for Saskatoon, Prince Albert, and Buffalo Pound WTRS were approximately 0.5 g, 0.05 g, and 0.035 g dry mass. These dosages were determined by trial and error as to remove a significant portion of the initial P without removing 100%. Total phosphorus was measured using a spectrophotometer (DR-4000, Hach Co., Loveland, CO) and the persulphate digestion and stannous chloride methods (4500-P B and 4500-P D) from the Standard Methods for the Examination of Water & Wastewater (APHA-AWWA-WEF 2005). Equilibrium appeared to occur after two days, as shown in Figure 3.4. Three days was chosen as the running time for the isotherm tests for a factor of safety.

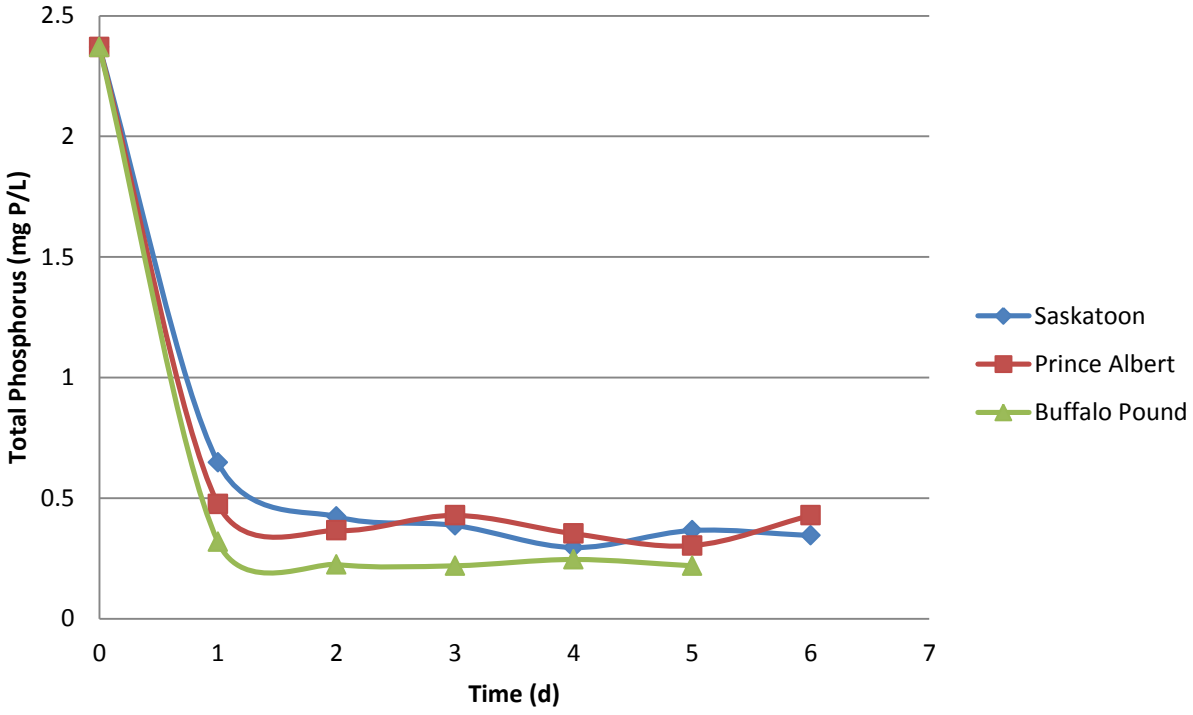

Figure 3.4 Preliminary test to determine time to equilibrium

3.3.2 Adsorption Isotherm

The isotherm test was performed using the jar apparatus. A constant mass of WTRS was mixed with 1000 mL of various concentrations of P-spiked solutions. Isotherm testing using P-spiked deionized water provides a bulk indication of the WTRS adsorption properties. Adsorption isotherms using a specific effluent the WTRS will be treating (i.e. wastewater and stormwater runoff) provides information specific to the collection period of the wastewater which is unique and not representative of all wastewaters and all conditions. Mixing was continuous until the time to equilibrium, determined to be three days from the preliminary study, was achieved. Testing was performed at room temperature and there was no pH adjustment.

A stock solution of 10 g P/L was made by adding 21.9 g of potassium phosphate [KH_2PO_4] (EM Science) to 500 mL of deionized water. Concentrations ranging from 1 to 6 mg P/L were created by adding varying volume of the 10 g P/L stock solution into jars filled with 1000 mL of deionized water. These concentrations represent typical domestic wastewater and stormwater runoff P concentrations (Table 2.6 and Table 2.12). The dry masses of Saskatoon, Prince Albert, and Buffalo Pound WTRS added were approximately 0.5 g, 0.05 g, and 0.035 g respectively as shown in Table 3.1. These dosages were determined from the preliminary equilibrium test and were used because at low phosphorus concentrations a significant amount of P was removed and as the initial P concentration increased less P was removed. This allowed for a broad range of P removal data for the isotherm models for the range of initial P concentrations tested (1-6 mg P/L). After equilibrium, the jars were removed and the solution filtered through 0.45 µm MCE filters (Fisher Scientific) then stored until the residual P concentration, C_e, was measured. Total phosphorus was measured using a spectrophotometer (DR-4000, Hach Co., Loveland, CO) and the persulphate digestion and stannous chloride methods (4500-P B and 4500-P D) from Standard Methods (APHA-AWWA-WEF 2005).

Table 3.1 Dry mass dosages of WTRS for isotherm tests

WTRS	Dry Mass (g)	
	Sample 1	Sample 2
Saskatoon	0.490	0.510
Prince Albert	0.051	0.051
Buffalo Pound	0.035	0.036

3.3.2.1 Adsorption Isotherm Analysis

The equilibrium concentrations for all batch adsorption experiments were fitted to the Langmuir and Freundlich adsorption isotherm equations (Equation 2.12 and Equation 2.14). The adsorption density of the WTRS at a given P concentration is determined by:

$$Q = \frac{(C_0 - C_e) \times V}{m} \qquad [3.1]$$

where C_0 and C_e are the initial and equilibrium phosphate concentrations (mg P/L), respectively, V is the volume of solution (L), and m is the mass of adsorbent (g).

The adsorption density achieved, Q, and the equilibrium concentrations, C_e, were determined based upon experimental measurements. Then the Langmuir and Freundlich isotherm parameters were determined by fitting the data to the linear forms of the Langmuir and Freundlich isotherm equations (Equation 2.13 and Equation 2.15). A plot of C_e vs C_e/Q provides values for the Langmuir isotherm parameters k and Q_{max} where Q_{max} is determined from the slope of the line and k from the y-intercept. A plot of log C_e and log Q provides values for the Freundlich isotherm parameters K_f and n where n is determined from the slope of the line and K_f from the y-intercept.

3.4 Wastewater Phosphorus Removal Batch Treatment Tests

3.4.1 Primary Effluent

Phosphorus removal treatment of wastewater was performed on primary effluent from the Saskatoon wastewater treatment plant using Sample 1 WTRS. Primary effluent was used as a surrogate for facultative lagoon wastewater. Saskatoon, Prince Albert, and Buffalo Pound WTRS were dosed into 6 L of wastewater in 10 L plastic buckets. Testing was performed at room temperature and there was no pH adjustment. Three dosage levels were determined using results from the isotherm tests. A dosage which theoretically removes P down to 0.5 mg P/L (referred to as the objective based dosage), a half dosage which is half the WTRS mass of the objective based dosage, and an exceeding dosage that will theoretically remove P down to 0.05 mg P/L were used for P treatment. The goal to remove P down to 0.5 mg P/L was chosen as that is the objective of the Saskatoon wastewater treatment plant for total P in their final effluent (SaskH2O 2012). The dosages of the WTRS are listed in Table 3.2.

Dosages to achieve a specific equilibrium phosphorus concentration are determined by using the constructed Langmuir adsorption isotherm (Equation 2.13). From the isotherm testing k and Q_{max} will be known. Inputting a desired C_e will determine Q. The mass of WTRS required to obtain a specific C_e can be determined by substituting Q, the initial concentration of the wastewater, C_0, the desired equilibrium concentration, C_e, and the volume of wastewater, V, into Equation 3.1.

Table 3.2 WTRS dosages for primary effluent P removal treatment

WTRS	WTRS Dose (g dry mass)		
	Objective Based (0.5 mg P/L target)	Half of Objective Based Dose	Exceeding (0.05 mg P/L target)*
Saskatoon	12.42	6.21	38.5
Prince Albert	1.07	0.58	3.40
Buffalo Pound	0.70	0.35	1.83

* The goal of the exceeding dose for Saskatoon WTRS was 0.1 mg P/L due to lack of originally sampled WTRS material

Six litres of wastewater were poured into 10 L plastic buckets. Dosages of WTRS were added to each bucket. Then the buckets were mixed using the jar test apparatus for 1 hour to simulate initial mixing in the field. After 1 hour the buckets were removed and covered with aluminum foil and the settled WTRS left undisturbed until equilibrium was reached. Once equilibrium was reached the wastewater was remixed for 1 hour to re-suspend the settled WTRS and then removed and covered until equilibrium was re-established. Samples of the wastewater were taken periodically to measure the remaining P concentration. Sampling occurred more frequently during the early stages of treatment as the majority of P was removed quickly. Samples of the wastewater, ranging between 100 to 200 mL, were withdrawn close to the surface as not to disturb the settled WTRS, and filtered through 0.45 µm MCE filters (Fisher Scientific), then stored until P was measured. Orthophosphate was measured using the stannous chloride method [4500-P D] (APHA-AWWA-WEF 2005) and a spectrophotometer (DR-4000, Hach Co., Loveland, CO). Total phosphorus was measured using the persulphate digestion and stannous chloride methods [4500-P B and 4500-P D] (APHA-AWWA-WEF 2005) and a spectrophotometer (DR-4000, Hach Co., Loveland, CO).

An unfiltered sample was taken of the raw wastewater, before remixing occurred, and at the end of the treatment. A sample of 15 mL was taken from every bucket to measure turbidity with a turbidimeter (Model 2100P, Hach Co., Loveland, CO). The pH was measured for a select few buckets using a pH probe (827 pH Lab, Metrohm, Switzerland). An extra 15 mL was sampled and mixed with the 15 mL from the turbidity sample for a total of 30 mL sample for the pH test.

3.4.2 Runoff Water

Phosphorus removal treatment was also performed on runoff water. Only Saskatoon and Buffalo Pound Sample 1 WTRS and agricultural runoff water were tested (see Section 4.1). Testing was performed at room temperature and there was no pH adjustment. Only a dosage which theoretically removes P down to 0.5 mg P/L was used. The dosages of the WTRS are listed in Table 3.3.

Table 3.3 WTRS dosages for runoff water P removal treatment

WTRS	WTRS Dose (g dry mass) for P Objective (0.5 mg P/L target)
Saskatoon	3.73
Buffalo Pound	0.21

The WTRS were dosed into 6 L of runoff water in 10 L plastic buckets. The buckets were mixed using the jar test apparatus for 1 hour. Then they were removed and covered with aluminum foil and the settled WTRS left undisturbed until equilibrium was reached. Once equilibrium was reached the water was remixed for 1 hour to re-suspend the settled WTRS and then removed and covered until equilibrium was re-established. The P removal in the runoff water tests did not behave in a similar manner to the wastewater tests. Therefore, the WTRS dosage was doubled, remixed for 1 hour, and sat for 1 day. Sampling, filtering, and turbidity and pH measurements were performed as specified for the wastewater treatment.

3.5 Desorption

Once the primary effluent wastewater treatment test was complete, the WTRS were collected and mixed with deionized water to evaluate the desorption process. The remaining wastewater, after sampling from the wastewater treatment, was decanted down to the settled solids. The settled solid sludge volume was measured with a graduated cylinder and poured back into its bucket. The bucket was refilled back to 6 L with deionized water. The 6 L solution was mixed manually and a 100 mL sample was taken. The sample was placed into a 150 mL flask and covered. The flask was placed on a reciprocal shaker and mixed at 150 RPM for 2 weeks. After 2 weeks the samples were taken off the shaker and filtered through 0.45 µm MCE filters (Fisher Scientific). The filtrate was stored at 4°C until the P content was measured. Orthophosphate and total phosphorus were measured as specified above.

3.5.1 Desorption Analysis

The percentage of P that desorbed off the settled P-loaded WTRS can be determined knowing the mass of P that was adsorbed and desorbed.

The mass of P adsorbed by the WTRS is determined by:

$$(C_{ww} - C_e) \times V_{ww} \quad [3.2]$$

where C_{ww} is the filtered total P concentration of the raw wastewater sample, C_e is the P equilibrium concentration of the wastewater sample after P removal treatment , and V_{ww} is the volume of wastewater used for P removal treatment (6 L).

The mass of P that desorbed off the WTRS after two weeks is determined by:

$$(C_{des} - C_{dil}) \times V_{dil} \quad [3.3]$$

where C_{des} is the P concentration of the wastewater sample after the two week desorption period, C_{dil} is the diluted P concentration of the wastewater and deionized water solution, and V_{dil} is the volume of the diluted wastewater solution (6 L).

3.6 Summary of Analytical Procedures

Turbidity was measured using a turbidimeter (Model 2100P, Hach, Co., Loveland, CO). pH was measured using a pH probe (827 pH Lab, Metrohm, Switzerland).

The analytical procedures for phosphorus were followed from Standard Methods for the Examination of Water and Wastewater (APHA-AWWA-WEF 2005). Orthophosphate was measured using the stannous chloride method (Method 4500-P D) and spectrophotometry (DR-4000, Hach Co., Loveland, CO) at a wavelength of 690 nm. The relative error of the stannous chloride method for orthophosphate concentrations of 100-7000 µg P/L is 28.7-4.3% (APHA-

AWWA-WEF 2005). Total phosphorus was measured by performing persulphate digestion (Method 4500-P B) for 35 minutes prior to the stannous chloride method and spectrophotometry. The relative error of the persulphate and stannous chloride method for total phosphorus concentrations of 210-10230 g P/L is 9.2-4.3% (APHA-AWWA-WEF 2005).

The analytical procedures for Al, Fe, and Ca measurements by atomic adsorption spectrophotometry (Model 5000, Perkin-Elmer, Inc., Waltham, MA) were followed from Standard Methods for the Examination of Water and Wastewater (APHA-AWWA-WEF 2005). Method 3111D was used to measure Al and method 3111B was used to measure Fe and Ca. Typical relative errors achieved using these methods for Al, Fe, and Ca are 8.4, 2.3, and 0.4%, respectively (APHA-AWWA-WEF 2005).

3.7 Quality Control and Quality Assurance

The jars for the jar testing apparatus, as well as storage jars, flasks, and beakers, were made of glass (Pyrex, Kimax) to minimize the adsorption of phosphorus onto the surface of equipment. All glassware used for the phosphorus experiments was acid washed, rinsed with deionized water, and then air dried prior to use.

Blanks were analyzed for the jar apparatus and wastewater treatment to observe if equipment was removing phosphorus from the samples. Duplicates were performed for pH measurements of the raw wastewater and the Al, Fe, and Ca extractions. Triplicates were performed for the TS and TSS tests, isotherm batch adsorption tests, wastewater P removal treatment (including pH and turbidity measurements), and desorption tests.

The turbidimeter (Model 2100P, Hach Co., Loveland, CO) was calibrated following Hach standards using 20, 100, and 800 NTU Formazin standards with a 4000 NTU Formazin stock solution. The pH probe (827 pH Lab, Metrohm, Switzerland) was calibrated using 4.01, 7.00, and 10.01 pH buffers. The turbidimeter and pH meter were calibrated at the beginning of each new wastewater sample set.

The spectrophotometer (DR-4000, Hach Co., Loveland, CO) was calibrated using four points and standard P solutions. The machine was checked periodically with standard P solutions and recalibrated if $R^2 < 0.99$. The atomic adsorption spectrophotometer (Model 5000, Perkin-Elmer, Inc., Waltham, MA) was calibrated using two points with standard solutions of the element being tested (Al, Fe, or Ca). It was constantly checked and adjusted using standard element solutions during testing.

Filtration of samples was through 0.45 µm filters as recommended by Standard Methods (APHA-AWWA-WEF 2005). Filters were rinsed thoroughly with deionized water prior to use to remove trace amounts of phosphorus.

3.8 Statistical Analysis

An adsorption plot of C_e and Q was constructed for the isotherm replicates where Q was determined using Equation 3.1. Each sample time and location consisted of triplicates of six dosages therefore the each WTRS sample set was comprised of 18 independent data points. The adsorption density, Q, of the isotherm replicates was tested using ANOVAs ($\alpha = 0.05$) to determine if they were statistically similar. Then the adsorption densities of the Sample 1 and Sample 2 isotherms for a given WTRS were analyzed using ANOVAs ($\alpha = 0.05$) to test if the two sample sets were statistically similar.

The linearized forms of the Langmuir and Freundlich isotherms (Equation 2.13 and Equation 2.15) were plotted with 95% confidence intervals. The linearized isotherms and confidence intervals were a function of x and y. The Langmuir isotherm was a function of C_e and C_e/Q while the Freundlich isotherm was a function of log C_e and log Q. A line of best fit was placed through the data and the R^2 value of the line was used as an indicator of the isotherms ability to model the adsorption behaviour of the water treatment residual solids.

ANOVAs ($\alpha = 0.05$) of the P concentrations of the P removal treatments of municipal primary wastewater effluent and agricultural runoff were performed to test if the replicates within each treatment were statistically similar. If similar, the P concentrations were averaged.

The performance (ability to predict Q as a function of C_e in comparison to measurements) of the Langmuir and Freundlich models developed was evaluated using the root mean squared error (RMSE). RMSE is a measure of the average error, weighted according to the square of the error. Its range is from 0 to infinity, with 0 being a perfect score. RMSE is determined by:

$$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(O_i - P_i)^2} \qquad [3.4]$$

where N is the number of Q data points, O_i is the observed (i.e. measured) Q at concentration $(C_e)i$, and P_i is the predicted Q (Langmuir or Freundlich) at concentration $(C_e)i$.

CHAPTER 4 Results and Discussion

4.1 Phosphorus Content of Wastewater and Runoff Water Sources

The pH and P concentration of the wastewater and agricultural runoff samples are listed in Table 4.1. The urban stormwater runoff samples collected from six stormwater retention ponds had orthophosphate concentrations ranging from below detection limits to approximately 0.20 mg P/L. These concentrations were deemed too low for WTRS testing and therefore testing using urban stormwater as a P source was removed from this study. The primary effluent and agricultural runoff contained typical P concentrations (Table 2.3 and Table 2.6). The unfiltered and filtered primary effluent total phosphorus content comprised approximately 78% and 94% orthophosphate, respectively while the unfiltered and filtered agricultural runoff comprised 60% and 67%, respectively. Approximately 73% of the total phosphorus in the primary effluent was soluble whereas typically 80% of total phosphorus in untreated domestic wastewater is soluble (Viessman et al. 2009).

Table 4.1 Wastewater and agricultural runoff water sample pH and P concentration (percent of total phosphorus that is orthophosphate is shown in brackets)

Water Source		PO_4^{3-} Concentration, mg P/L (% of total)			
		Unfiltered		Filtered	
	pH	Ortho-P	Total-P	Ortho-P	Total-P
Saskatoon Primary Effluent	8.43	9.13 (78)	11.66	7.92 (94)	8.46
Agricultural Runoff Pond	8.40	2.06 (60)	3.45	1.92 (67)	2.86

4.2 Total Solids and Total Suspended Solids of WTRS

A summary of the total solids and total suspended solids of the decanted WTRS samples collected is presented in Table 4.2. The percent solids of the WTRS slurries ranged approximately from less than 1% to 7%. Alum coagulation sludge withdrawn from sedimentation basins is typically 1-2% solids (Viessman et al. 2009). Gravity thickening of settled sludge from coagulation can produce solids content of 2-6% for alum sludge, up to 10% for alum-lime sludge, and 10-20% for iron-lime sludge (Viessman et al. 2009).

Table 4.2 Total solids and total suspended solids of WTRS

WTRS	Average Mass Concentration (g WTRS/L)			
	Sample 1		Sample 2	
	TS	TSS	TS	TSS
Saskatoon	60.7/210	*/207	67.5	68.1
Prince Albert	34.0	37.3	26.3	25.5
Buffalo Pound	7.03	6.94	7.80	7.17

Note: Multiple values listed if multiple buckets of WTRS were used
*TSS test of Bucket 1 Saskatoon Sample WTRS was not performed

4.3 Elemental Composition

A summary of the Al, Fe, and Ca content and pH of the WTRS samples collected and utilized in the research are presented in Table 4.3 (see Appendix B for the results of the replicate measurements). Saskatoon WTRS had the highest Fe content ranging between 55.2-55.8 g/kg while Buffalo Pound had the highest Al content ranging between 56.0-67.2 g/kg. Saskatoon and Prince Albert had higher Ca content due to lime softening and pH control. The summer and fall sampling times appeared to have little effect on the Al, Fe, and Ca content however the collection period may not have sampled the most significant seasonal changes in source water quality. The Al, Fe, and Ca content of the WTRS were slightly higher for the fall samples. The water treatment plants may have adjusted the coagulant doses to treat higher suspended solids content of the source water caused by a storm event or upstream activities. Buffalo Pound had high chemical dosages throughout 2011 in part due to the Moose Jaw River flooding into Buffalo Pound Lake (Buffalo Pound Water Administration Board 2011). Low background concentrations of Al, Fe, and Ca are present in each WTRS sample originating from the environment and source water.

Table 4.3 Al, Fe, and Ca content of Sample 1 and Sample 2 WTRS

	WTRS					
	Saskatoon		Prince Albert		Buffalo Pound	
Coagulant	Ferric sulphate		Alum		Alum	
Sample	1	2	1	2	1	2
pH	8.15	8.24	7.81	7.83	5.98	7.25
Al_{ox} (g/kg)	1.12	1.46	41.8	46.7	56.0	67.2
Fe_{ox} (g/kg)	55.2	55.8	1.29	0.98	0.52	2.22
Ca (g/kg)	34.3	35.2	38.1	37.5	6.3	12.0

4.4 Phosphorus Adsorption in Spiked Samples

The phosphorus adsorption test and isotherm model fitting results for each of the WTRS materials investigated are presented in the following sections.

4.4.1 Saskatoon WTRS Phosphorus Adsorption in Spiked Samples

The Saskatoon adsorption test results are presented in Figure 4.1. The Sample 1 and Sample 2 adsorption isotherms were not statistically different (see Appendix C for ANOVA statistical testing results). The Langmuir isotherm model provided a good linear fit (R^2 = 0.97 and 0.99) to the transformed adsorption data (see Equation 2.13) of the Saskatoon WTRS Sample 1 (Figure 4.2) and Sample 2 (Figure 4.3). The Freundlich isotherm model also provided a linear fit (R^2 = 0.86 and 0.87) to the log transformed adsorption data (see Equation 2.15) for the Saskatoon WTRS Sample 1 (Figure 4.4) and Sample 2 (Figure 4.5). The Langmuir and Freundlich isotherm models both reasonably predict Q (Figure 4.6 and Figure 4.7) within the bounds of the observed data set with RMSE ranging from 0.40 to 0.68. The Q_{max} for Sample 1 was 7.37 mg P/g solid and 6.41 mg P/g solid for Sample 2. The Q_{max} were similar which was expected since the Fe and Ca content were similar (Table 4.3).

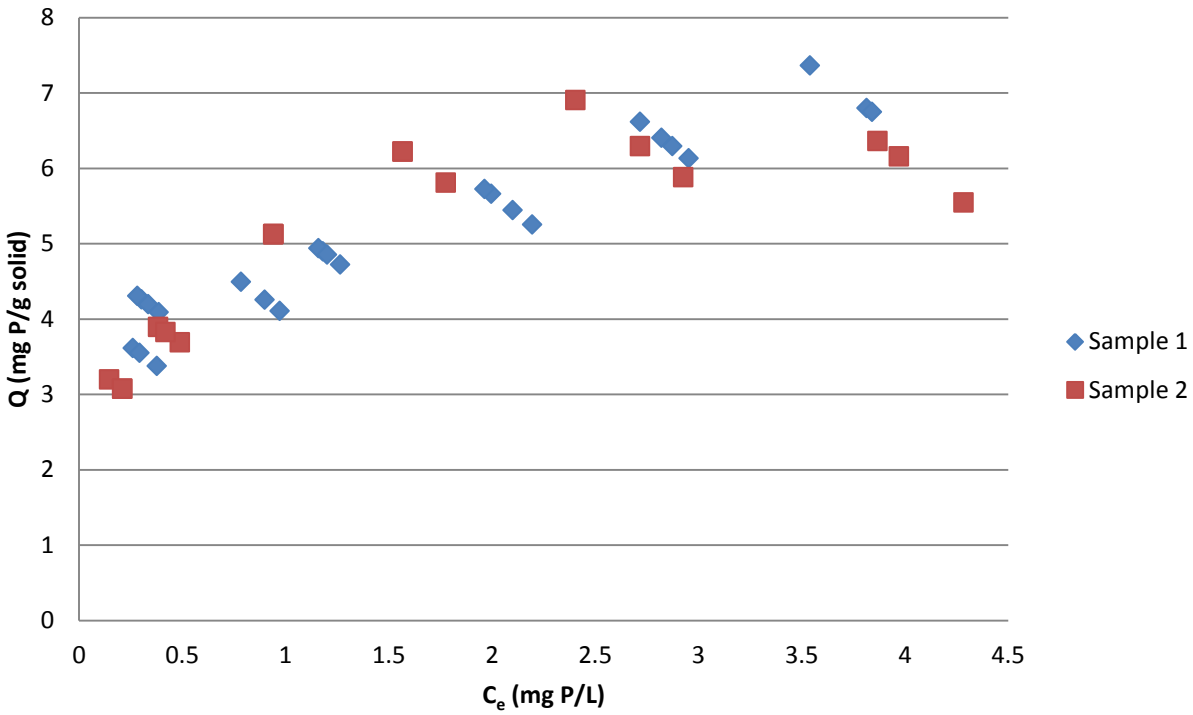

Figure 4.1 Adsorption test results for Saskatoon WTRS

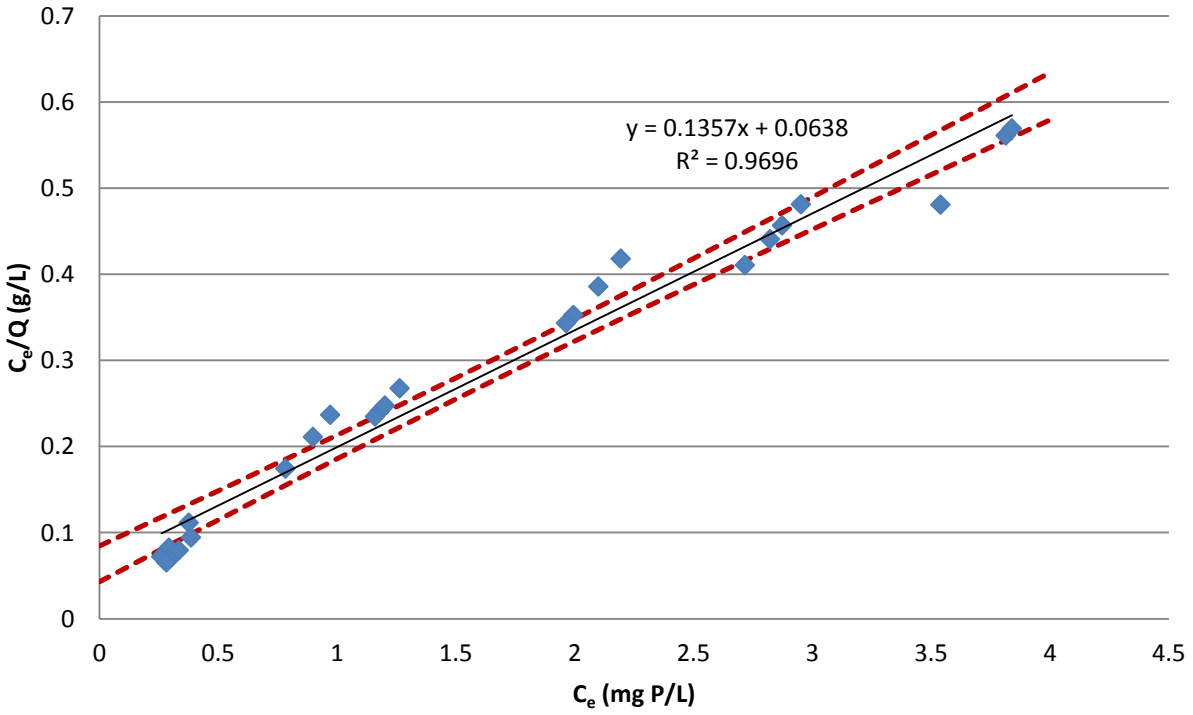

Figure 4.2 Linearized Langmuir isotherm model for Saskatoon WTRS Sample 1 (95% confidence interval)

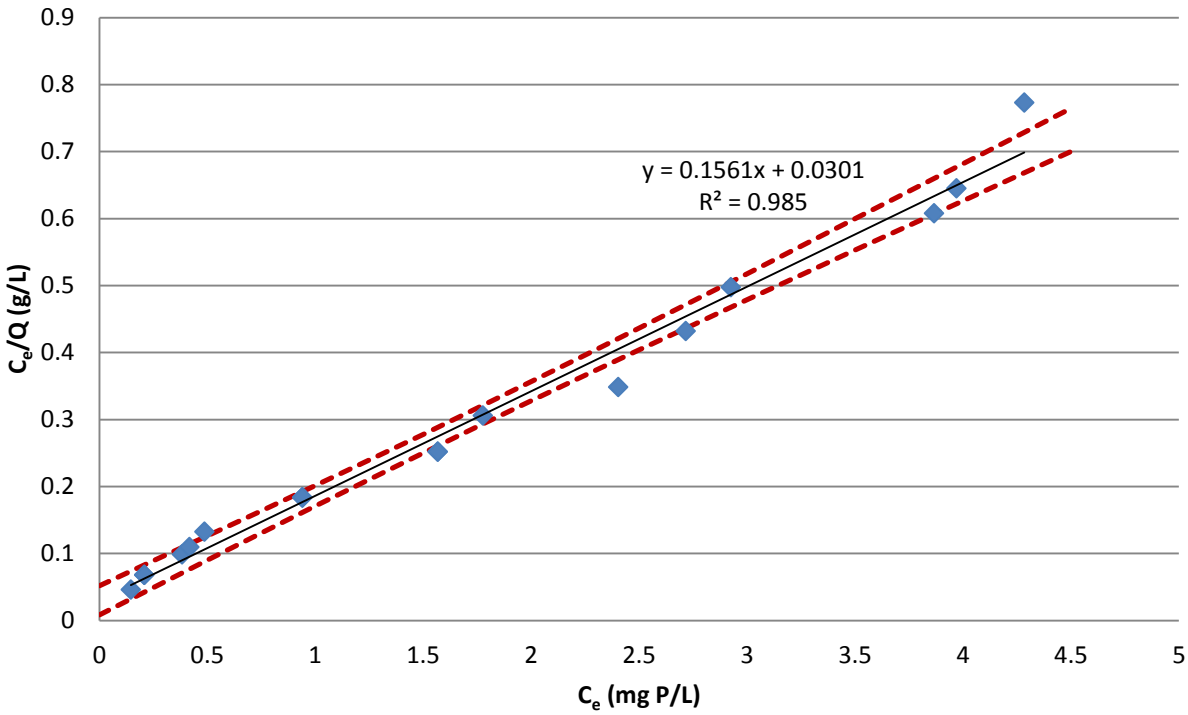

Figure 4.3 Linearized Langmuir isotherm model for Saskatoon WTRS Sample 2 (95% confidence interval)

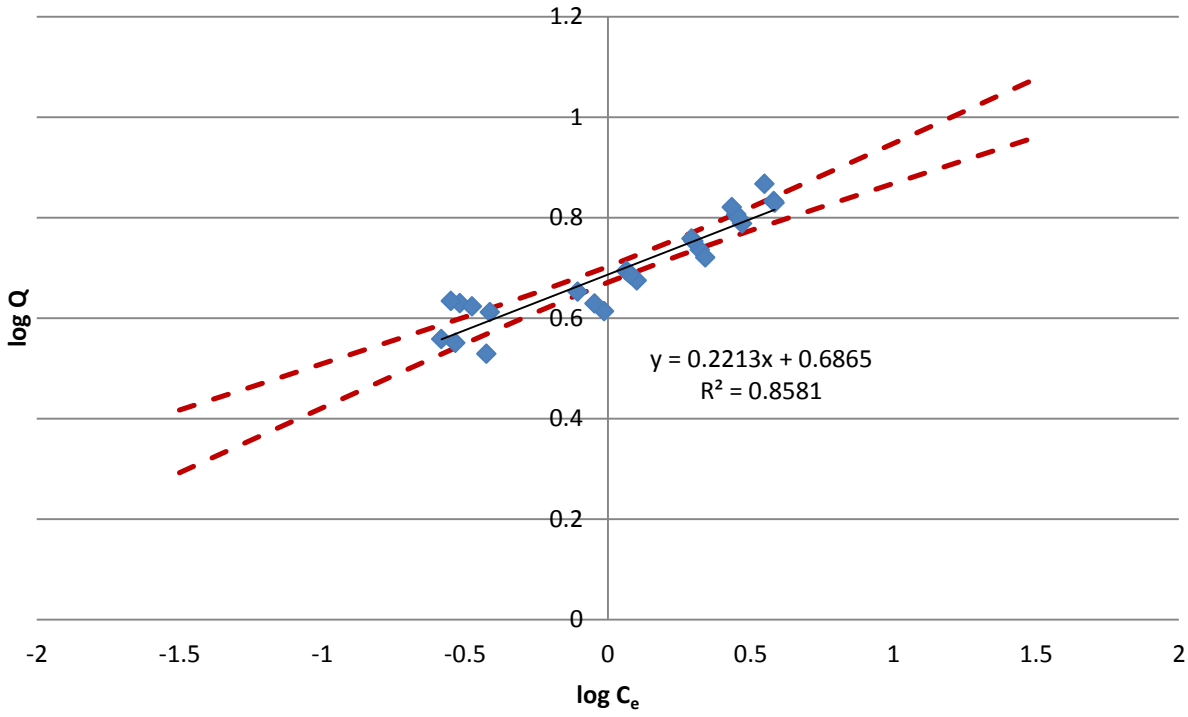

Figure 4.4 Linearized Freundlich isotherm model for Saskatoon WTRS Sample 1 (95% confidence interval)

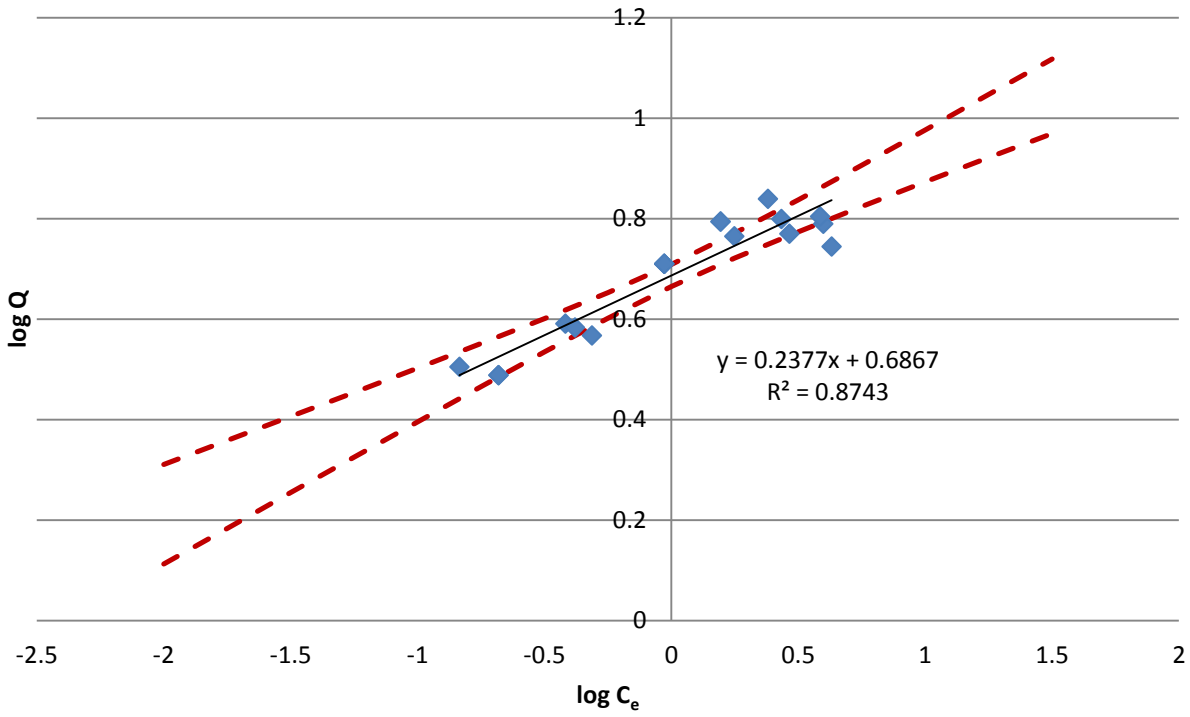

Figure 4.5 Linearized Freundlich isotherm model for Saskatoon WTRS Sample 2 (95% confidence interval)

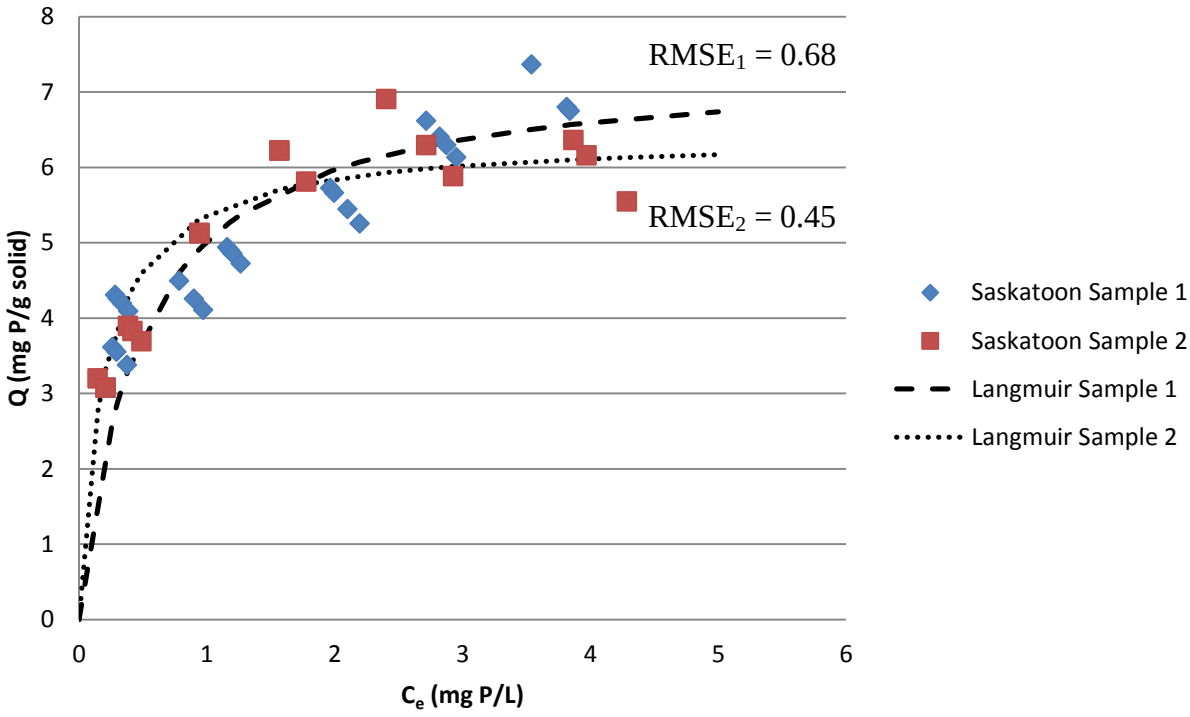

Figure 4.6 Saskatoon WTRS Langmuir adsorption model and observations

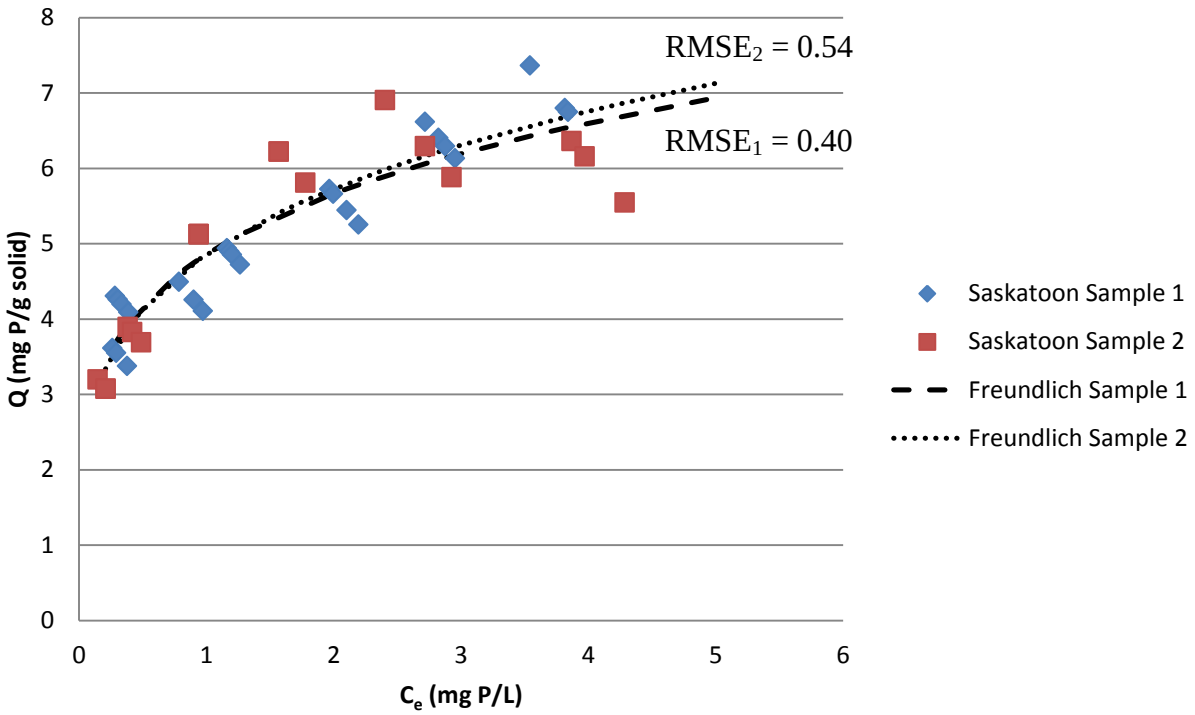

Figure 4.7 Saskatoon WTRS Freundlich adsorption model and observations

4.4.2 Prince Albert WTRS Phosphorus Adsorption in Spiked Samples

The Prince Albert adsorption test results are presented in Figure 4.8. The Sample 1 and Sample 2 adsorption isotherms were not statistically different (see Appendix C for ANOVA statistical testing results). The Langmuir isotherm model produced a good linear fit (R^2 = 0.98 and 0.99) to the transformed adsorption data of the Prince Albert WTRS Sample 1 (Figure 4.9) and Sample 2 (Figure 4.10). The Freundlich isotherm produced a poor linear fit (R^2 = 0.69) to the log transformed adsorption data for Sample 1 (Figure 4.11) but a good linear fit (R^2 = 0.91) for Sample 2 (Figure 4.12). The Langmuir isotherm model less accurately predicts Q (Figure 4.13) within the bounds of the data set with RMSE ranging from 4.5 to 5.9 compared to the Freundlich isotherm model (Figure 4.14) with RMSE ranging from 2.6 to 3.3. The Q_{max} for Sample 1 was 53.5 mg P/g solid and 70.4 mg P/g solid for Sample 2. The difference in Q_{max} may be due to Sample 2's higher Al content (Table 4.3). There may also have been other species contained within the Sample 2 WTRS that contributed to P removal.

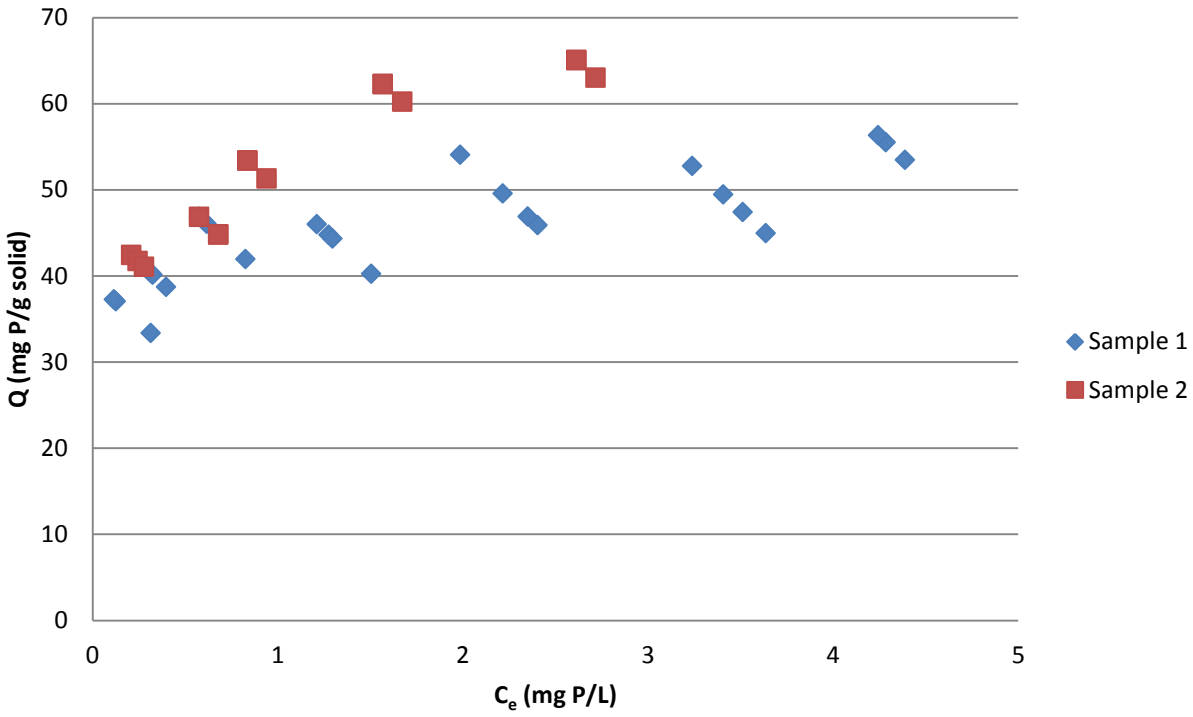

Figure 4.8 Adsorption test results for Prince Albert WTRS

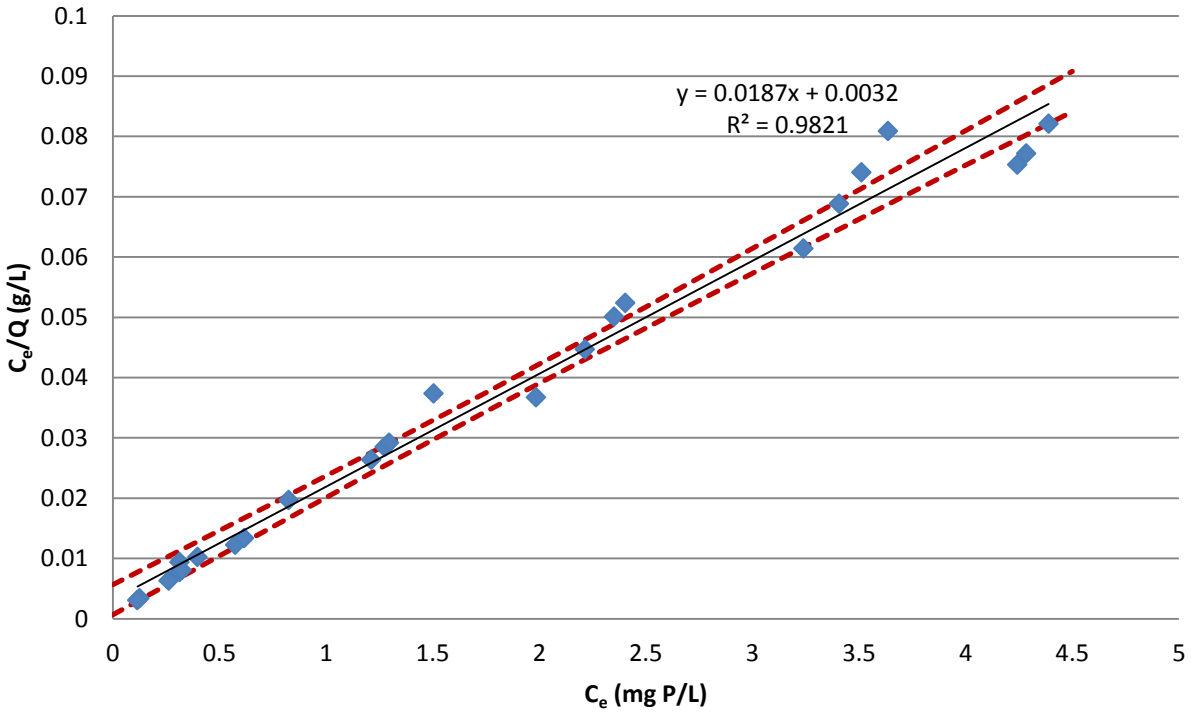

Figure 4.9 Linearized Langmuir isotherm model for Prince Albert WTRS Sample 1 (95% confidence interval)

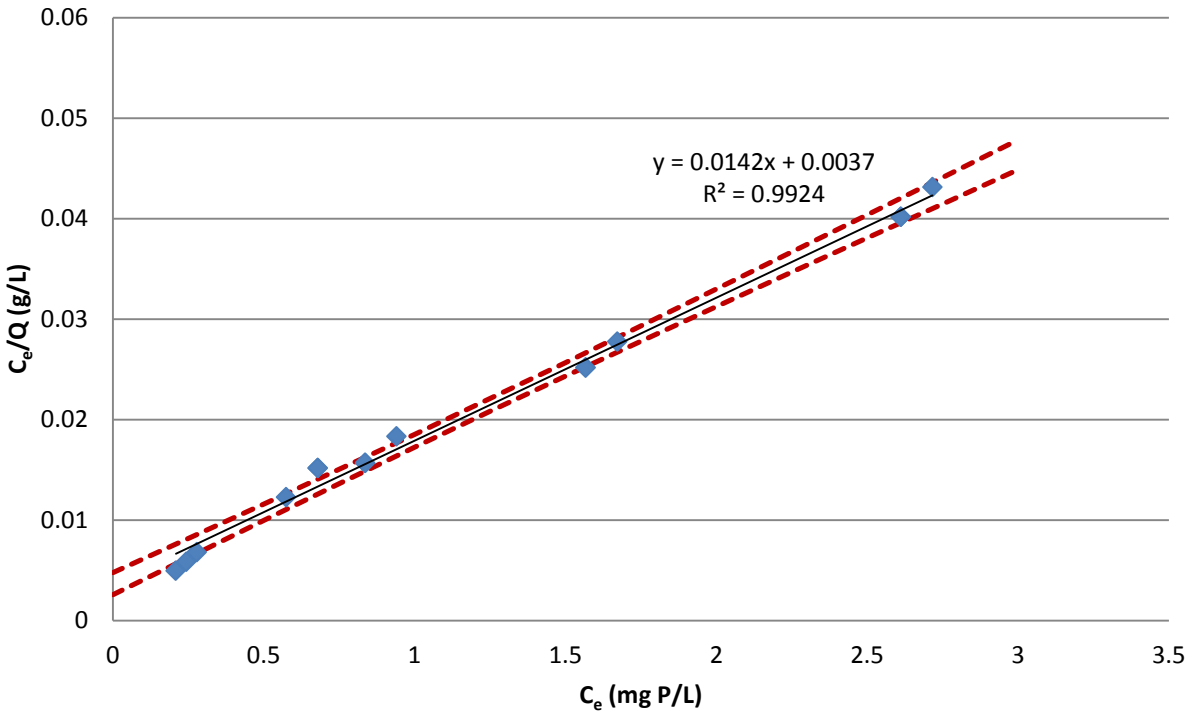

Figure 4.10 Linearized Langmuir isotherm model for Prince Albert WTRS Sample 2 (95% confidence interval)

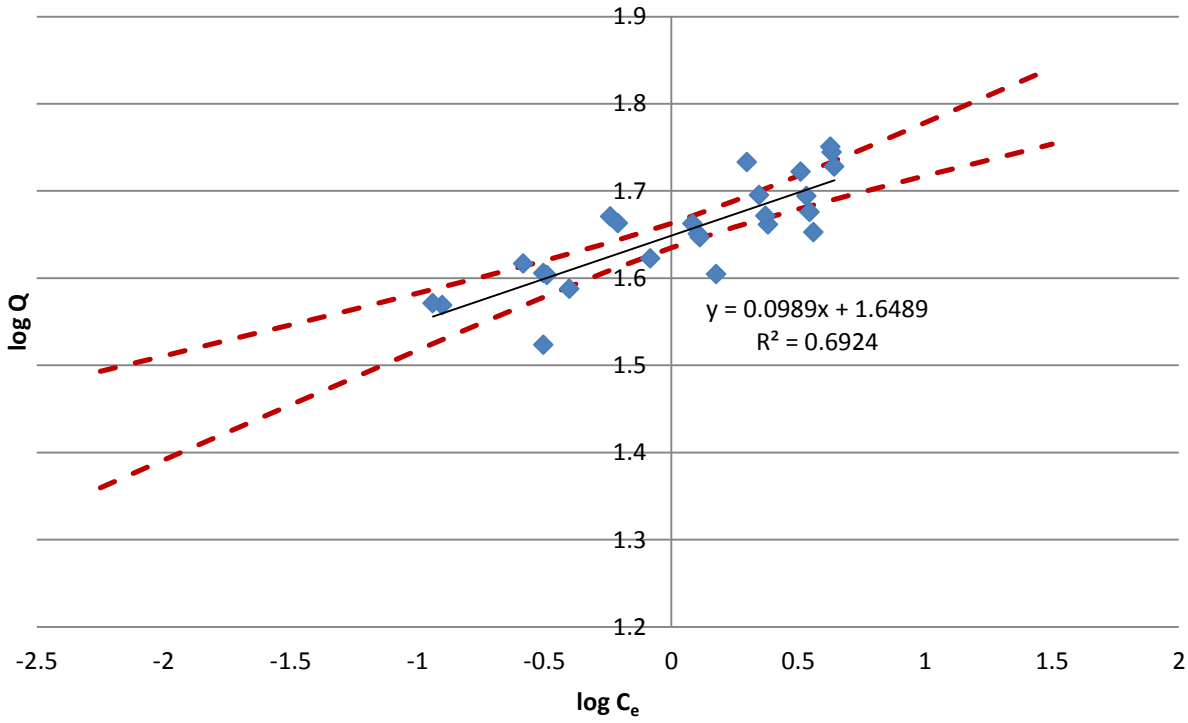

Figure 4.11 Linearized Freundlich isotherm model for Prince Albert WTRS Sample 1 (95% confidence interval)

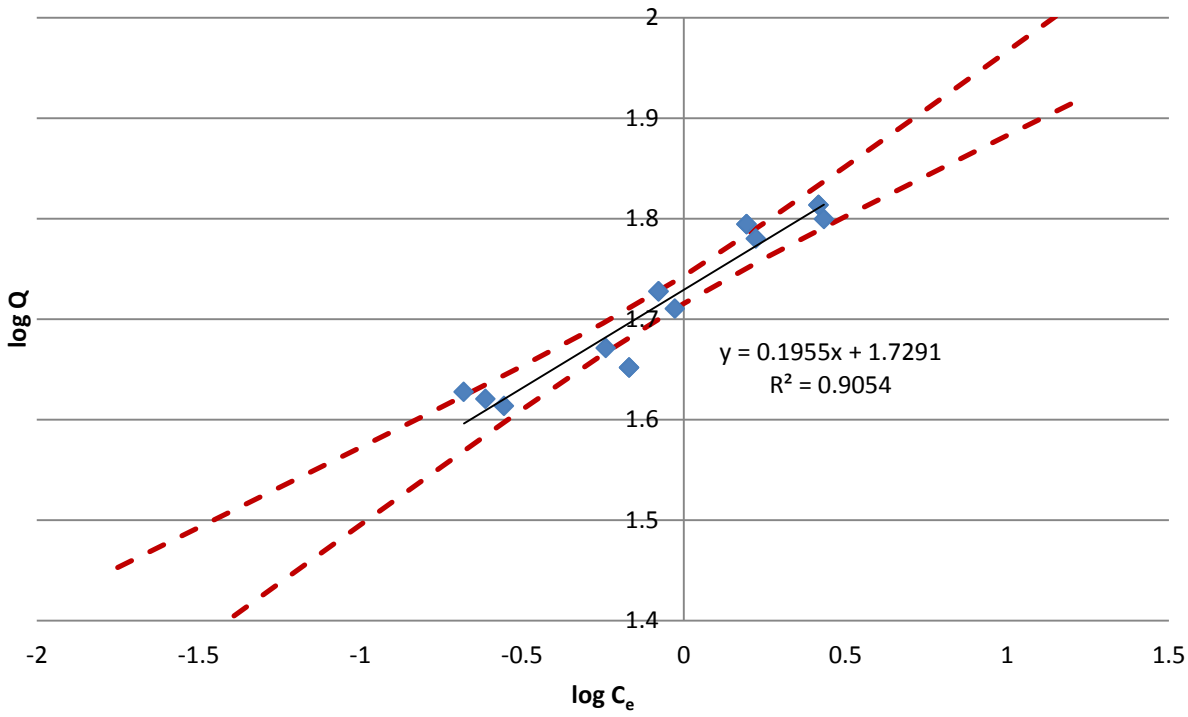

Figure 4.12 Linearized Freundlich isotherm model for Prince Albert WTRS Sample 2 (95% confidence interval)

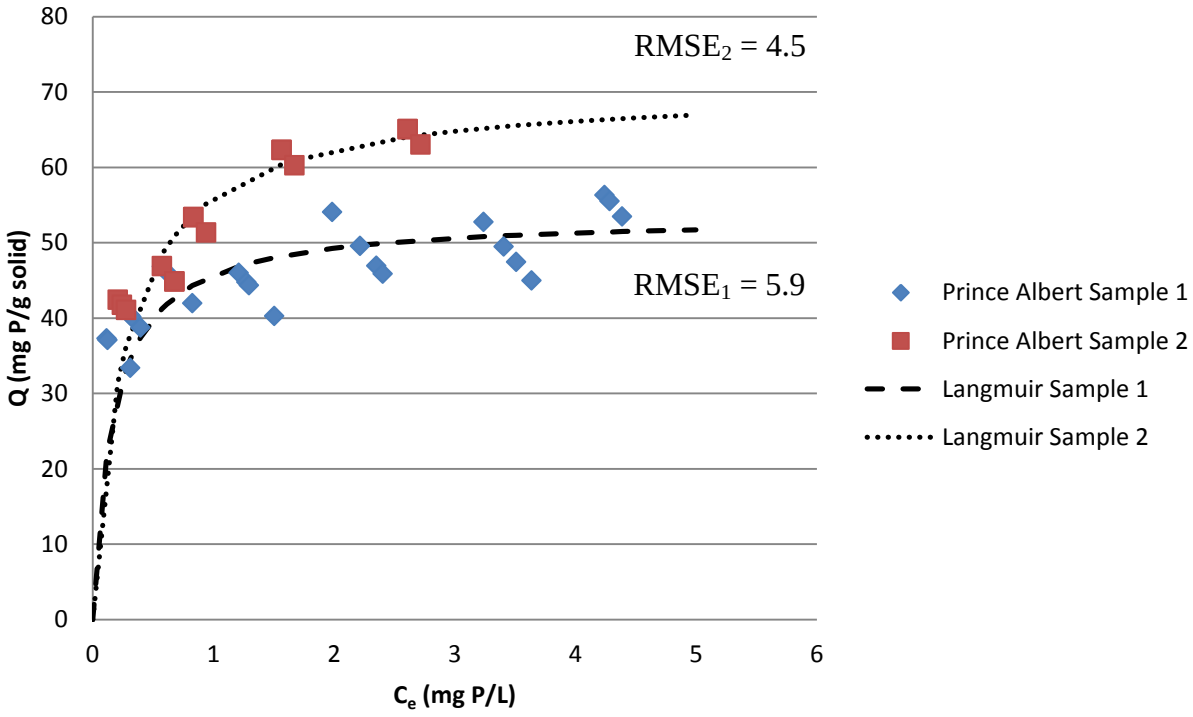

Figure 4.13 Prince Albert WTRS Langmuir adsorption model and observations

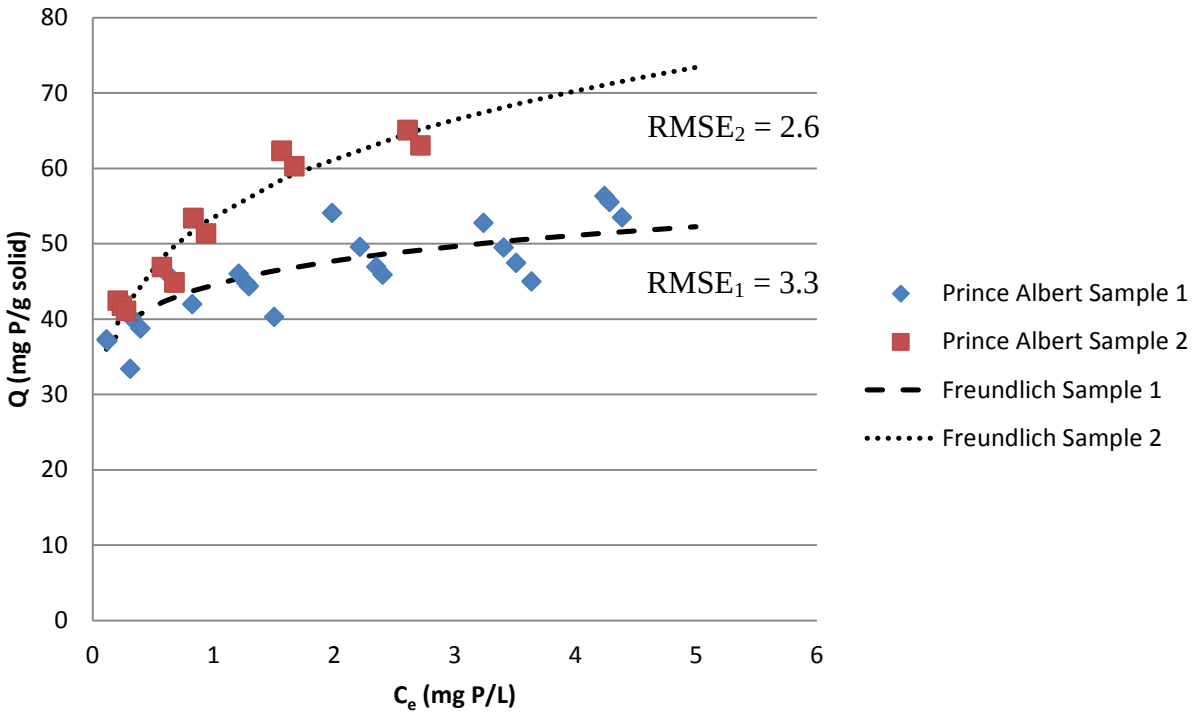

Figure 4.14 Prince Albert WTRS Freundlich adsorption model and observations

4.4.3 Buffalo Pound WTRS Phosphorus Adsorption in Spiked Samples

The Buffalo Pound adsorption test results are presented in Figure 4.15. The Sample 1 and Sample 2 adsorption isotherms were not statistically different (see Appendix C for ANOVA statistical testing results). The Langmuir isotherm model provided a good linear fit (R^2 = 1.00 and 0.97) to the transformed adsorption of the Buffalo Pound WTRS Sample 1 (Figure 4.16) and Sample 2 (Figure 4.17). The Freundlich isotherm produced a linear fit (R^2 = 0.82) to the log transformed adsorption data for Sample 1 (Figure 4.18) but a poor linear fit (R^2 = 0.63) for Sample 2 (Figure 4.19). The Langmuir isotherm model less accurately predicts Q (Figure 4.20) within the bounds of the data set for Sample 1 with RMSE of 4.9 compared to the Freundlich isotherm model (Figure 4.21) with RMSE of 2.3. The Langmuir and Freundlich isotherm models equally predict Q (Figure 4.20 and Figure 4.21) within the data set range for Sample 2 with RMSE ranging from 6.8 to 7.0. The Q_{max} for Sample 1 was 78.1 mg P/g solid and 82.0 mg P/g solid for Sample 2. Sample 2 did have a higher Al content (Table 4.3) however the Q_{max} were similar.

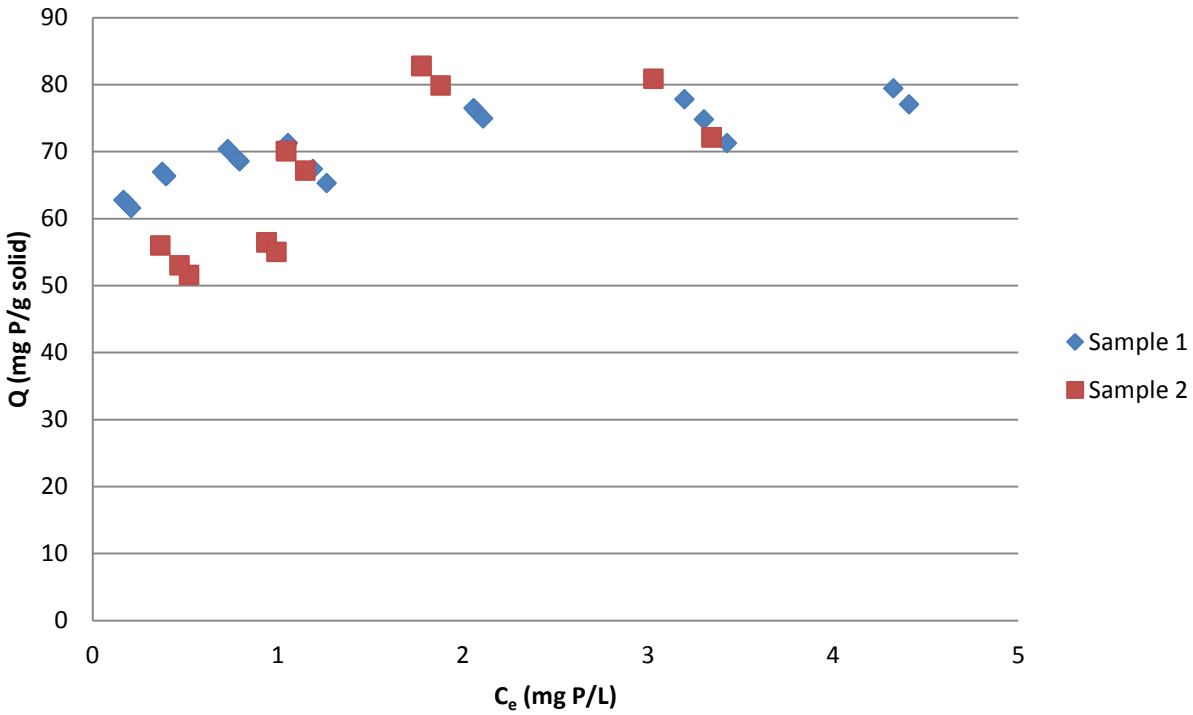

Figure 4.15 Adsorption test results for Buffalo Pound WTRS

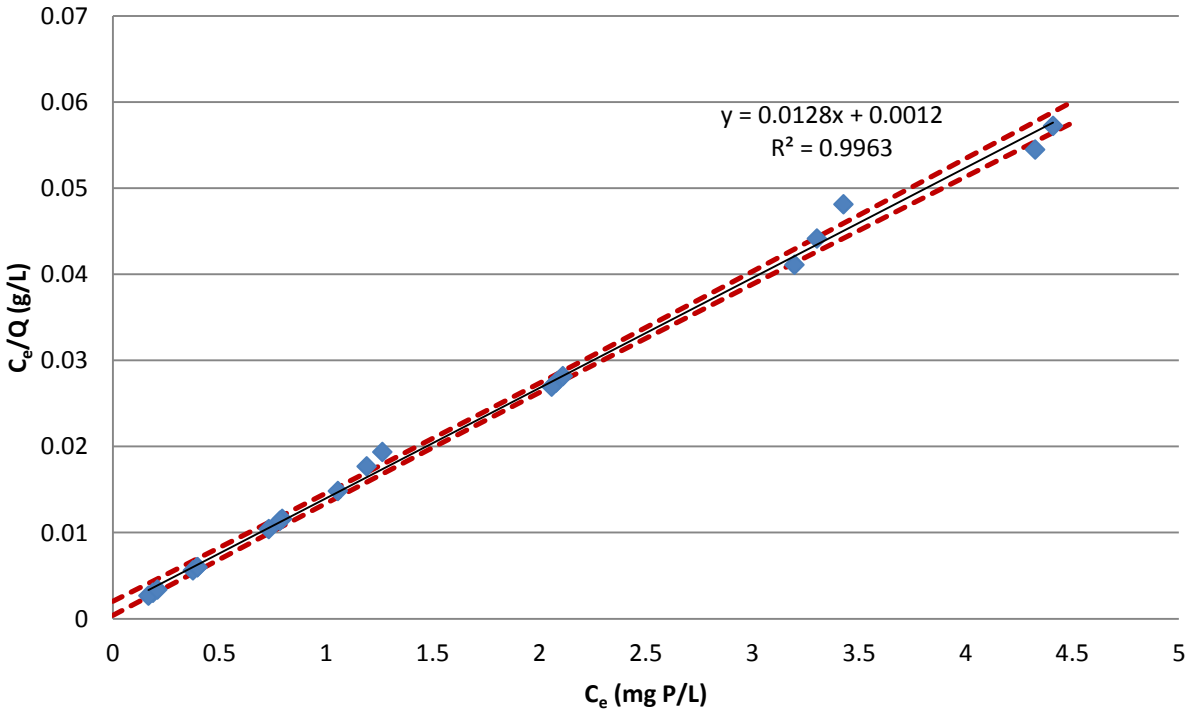

Figure 4.16 Linearized Langmuir isotherm model for Buffalo Pound WTRS Sample 1 (95% confidence interval)

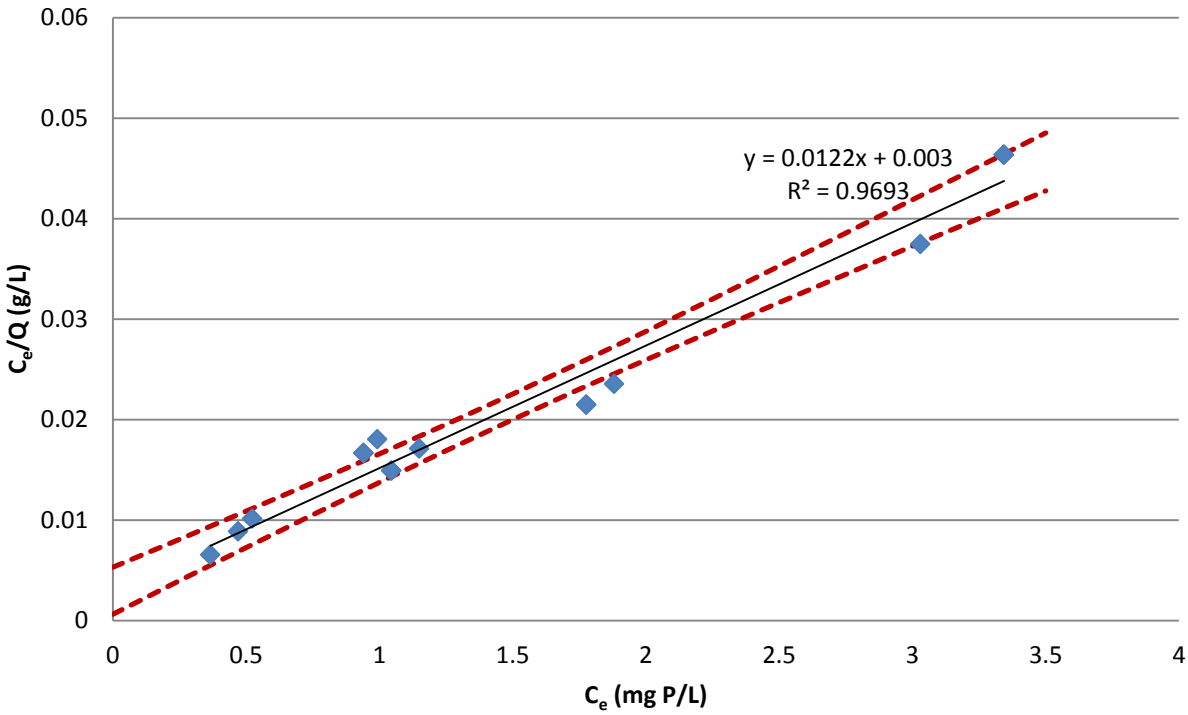

Figure 4.17 Linearized Langmuir isotherm model for Buffalo Pound WTRS Sample 2 (95% confidence interval)

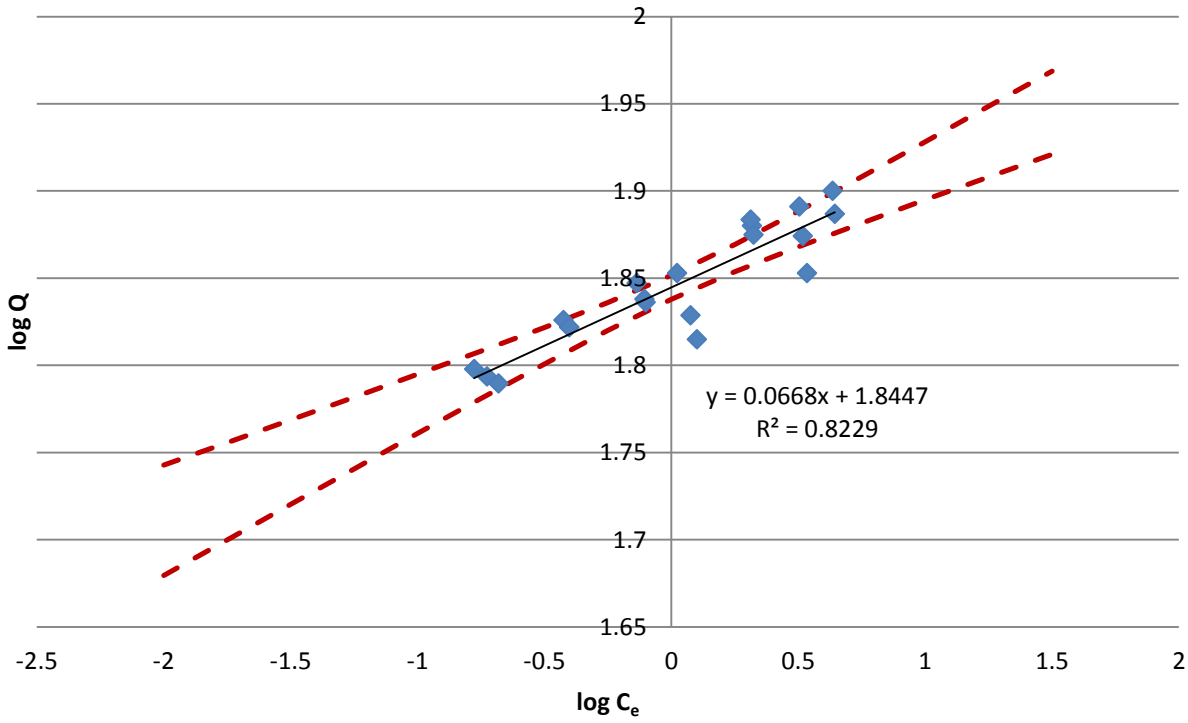

Figure 4.18 Linearized Freundlich isotherm model for Buffalo Pound WTRS Sample 1 (95% confidence interval)

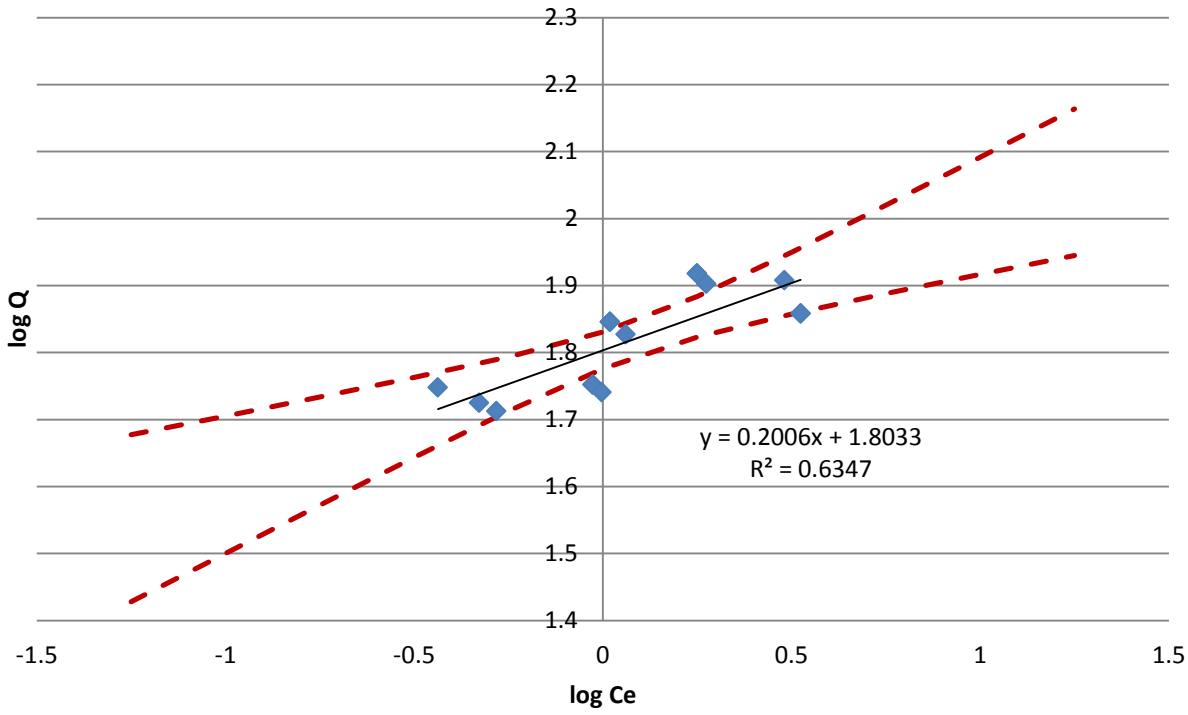

Figure 4.19 Linearized Freundlich isotherm model for Buffalo Pound WTRS Sample 2 (95% confidence interval)

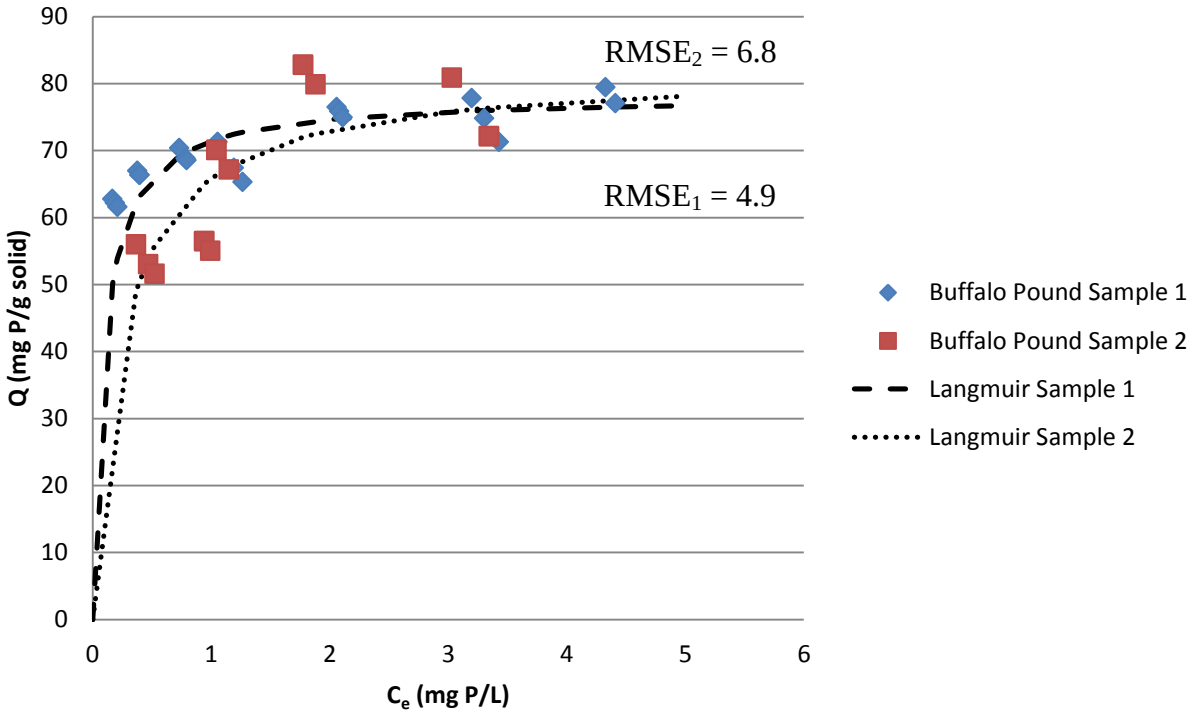

Figure 4.20 Buffalo Pound WTRS Langmuir adsorption model and observations

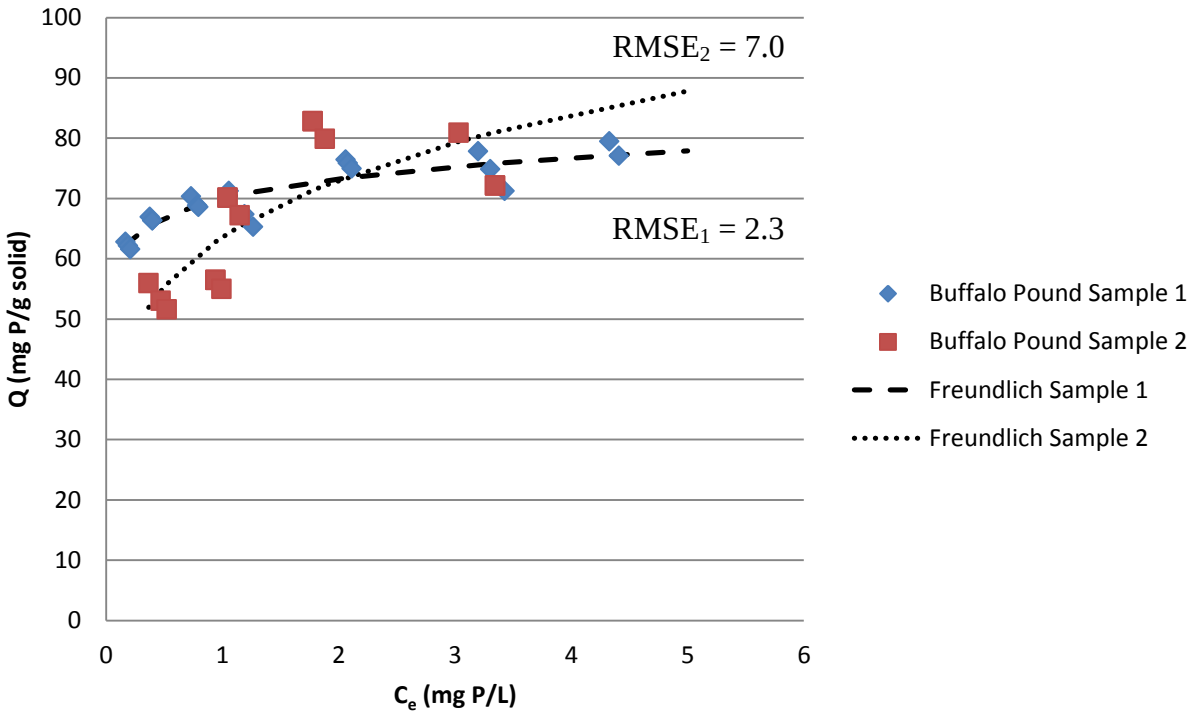

Figure 4.21 Buffalo Pound WTRS Freundlich adsorption model and observations

4.4.4 Summary of Phosphate Adsorption in Spiked Samples

The P adsorption behaviour of the WTRS in spiked P samples prepared with deionized water was modelled using the Langmuir and Freundlich linearized isotherm models. The Langmuir model fit the transformed data well for phosphate adsorption on the alum and iron residuals with R^2 ranging from 0.97 to 1.00 for all WTRS (Table 4.4). The Freundlich model had not as good a fit to the log transformed data with R^2 ranging from 0.63 to 0.87 for all WTRS (Table 4.4). For the Freundlich isotherm model the fit to the Fe WTRS log transformed data was more consistent between the Sample 1 and Sample 2 than the Al WTRS log transformed data. Typically, the Freundlich model was a more accurate prediction model (based upon lower RMSE) for Q vs C_e within the range of the data set. However, the Langmuir model is expected to be a better overall model of the P adsorption behaviour of WTRS based upon the residuals exhibiting an adsorption saturation and the significant R^2 of the linear fit of the transformed data.

Sample 1 WTRS achieved Q_{max} in the following order: Buffalo Pound (78.1 mg P/g solid) > Prince Albert (53.5 mg P/g solid) > Saskatoon (7.37 mg P/g solid). Sample 2 WTRS resulted in

similar Q_{max} results in the following order: Buffalo Pound (82.0 mg P/g solid) > Prince Albert (70.4 mg P/g solid) > Saskatoon (6.41 mg P/g solid). The Q_{max} results for Sample 1 and Sample 2 WTRS were statistically similar (see Appendix C for statistical results). A summary of test results and Langmuir and Freundlich constants are shown in Table 4.4. Detailed results of the phosphorus adsorption in spiked P samples in deionized water experiments can be found in Appendix C.

Table 4.4 Langmuir and Freundlich adsorption isotherm test results

	WTRS					
	Saskatoon		Prince Albert		Buffalo Pound	
Coagulant	Ferric sulphate		Alum		Alum	
Initial pH	≈7		≈7		≈7	
Sample	1	2	1	2	1	2
WTRS pH	8.15	8.24	7.81	7.83	5.98	7.25
Dry mass of WTRS (g)	0.49	0.51	0.051	0.051	0.035	0.036
Langmuir						
Q_{max} (mg P/g solid)	7.37	6.41	53.5	70.4	78.1	82.0
k (L/mg)	2.13	5.19	5.91	3.84	10.7	4.07
Linearized Langmuir R^2	0.97	0.99	0.98	0.99	1.00	0.97
Q vs C_e RMSE	0.68	0..45	5.9	4.5	4.9	6.8
Freundlich						
K_F (L/g)	4.86	4.86	44.6	53.6	69.9	63.6
N	4.52	4.21	10.1	5.12	15.0	4.98
Linearized Freundlich R^2	0.86	0.87	0.69	0.91	0.82	0.63
Q vs C_e RMSE	0.40	0.54	3.3	2.6	2.3	7.0

Note: Particle sizes unknown since WTRS were applied in sludge form and unaltered after collection. The particles sizes will not be equivalent between WTRS

A summary of the WTRS Al, Fe, and Ca molar concentrations and the Langmuir Q_{max} parameters obtained from the batch phosphate adsorption in spiked sample tests is presented in Table 4.5. Aluminum based water treatment residual solids appeared to be a better adsorbent of P compared to iron based residuals based on the adsorption densities. When comparing Al-based WTRS to Fe-based WTRS, the Al-based performed better on a mass of P adsorbed per mass of metal basis (Makris et al. 2005a; Elliott et al. 2002). However, on a mass of P adsorbed per mol of metal species basis Gibbons (2009) found Fe WTRS to be slightly more effective. The Fe-based WTRS may have had different physical and chemical characteristics than the Al-based

WTRS that affected phosphorus adsorption. The particle sizes were unknown and would not be the same which would impact their phosphorus adsorption capacities. The Al-based WTRS may also have had a more porous structure that provided more surface area for phosphorus diffusion and adsorption.

Table 4.5 Summary of WTRS Al, Fe, and Ca molar concentrations and Langmuir parameters

	WTRS					
	Saskatoon		Prince Albert		Buffalo Pound	
Coagulant	Ferric sulphate		Alum		Alum	
Sample	1	2	1	2	1	2
Al_{ox} (mol/kg)	0.04	0.05	1.55	1.73	2.07	2.49
Fe_{ox} (mol/kg)	0.99	1.00	0.02	0.02	0.01	0.04
Ca (mol/kg)	0.86	0.88	0.95	0.94	0.16	0.30
Q_{max} (mg P/g WTRS)	7.37	6.41	53.5	70.4	78.1	82.0
k (L/mg)	2.13	5.19	5.91	3.84	10.7	4.07

Adsorption of P by WTRS is affected by the crystallinity where amorphous Al and Fe are more effective compared to crystalline forms (Elliott et al. 2002). Non-crystalline oxides are often measured by oxalate-extraction (McKeague et al. 1971). The Sample 1 and Sample 2 oxalate-extractable Al and Fe (Al_{ox} + Fe_{ox}) content of the Saskatoon, Prince Albert, and Buffalo Pound WTRS were 1.03, 1.05, 1.57, 1.75, 2.08, and 2.53 mol kg^{-1}, respectively. Therefore, it was expected that the Q_{max} order would be Buffalo Pound > Prince Albert > Saskatoon. This was confirmed with Sample 1 and Sample 2 Saskatoon, Prince Albert, and Buffalo Q_{max} values obtained in this study of 7.37, 6.41, 53.5, 70.4, 78.1, and 82.0 mg P/g WTRS, respectively.

The Ca content of the Saskatoon and Prince Albert WTRS was expected to contribute to P removal likely by adsorption and Ca-P precipitates (Elliott et al. 2002). However, the calcium content of the WTRS samples tested were low compared to Ca-based WTRS from full lime softening processes which have been shown to be effective at removing phosphorus (Gibbons 2009; Elliott et al. 2002). Calcium appeared to be less effective at removing P based upon the Saskatoon WTRS high Fe and Ca content yet low Q_{max} compared to Prince Albert and Buffalo Pound. Also, Buffalo Pound WTRS were more effective with similar Al content as Prince Albert yet low Ca content.

The Buffalo Pound WTRS had approximately 25% more mass of aluminum per mass of WTRS but negligible Ca compared to the Prince Albert WTRS. The Buffalo Pound Q_{max} was approximately 25% higher than the Prince Albert Q_{max}. This suggests the Ca in the WTRS tested in this study had little impact on the P adsorption by the WTRS. Gibbons (2009) and Elliott et al. (2002) found Ca-based WTRS from full lime softening processes were effective at removing P and were equivalent or better than Al- and Fe-based WTRS based upon mass of P adsorbed per mass of metal species. In contrast the Ca content of the WTRS samples collected for this study did not influence P removal significantly.

The maximum phosphorus adsorption capacities obtained in this study were typically significantly higher than those of other WTRS (Table 4.6). The testing conditions (pH, particle size, initial P concentration, equilibrium time) directly impact the Q_{max} results of the WTRS (see Table 2.15 for testing conditions of the studies). The particle sizes of the Saskatoon, Prince Albert, and Buffalo Pound WTRS were unknown which is an important factor since Q_{max} increases with decreasing particle size (Zhao et al. 2007; Mortula 2006; Dayton and Basta 2005a; Novak and Watts 2005). The WTRS tested in this study were applied in slurry form and would have an amorphous structure as they were never dried and clumped together. Consequently the particle sizes are expected to be small in comparison to dried and crushed WTRS. The concentrations used in this study (1-6 mg P/L) reflect typical P concentrations in wastewater effluent (Table 2.6). Hence the Q_{max} values of this study may be a better representation of adsorption capacity under typical P concentration and WTRS non-crystalline structure conditions.

Table 4.6 Maximum phosphorus adsorption capacities of several WTRS

Coagulant	Q_{max} (mg P/g solid)	Reference
Alum	53.5-82.0	This research
Ferric sulphate	6.41-7.37	This research
Alum	73-150	Novak and Watts 2005
Alum	3.33	Razali et al. 2007
Alum	8.16	Kim et al. 2003
Alum	3.5	Yang et al. 2006b
Alum	0.097-0.11	Huang and Chiswell 2000
Alum	12.5	Ippolito et al. 2003
Alum	0.3-5.14	Dayton et al. 2003
Alum	1.84-29.5	Dayton and Basta 2005a
	10.4-37.0	"
Alum	7.5-10	Makris et al. 2005a
Alum	1.03-1.11	Gibbons 2009
Lime	1.39	"
Ferric sulphate	2.96	"
Alum	31.9	Babatunde and Zhao 2010
	10.2	"

4.5 Ammonium Oxalate-Extractable Al and Fe and Maximum Phosphorus Adsorption Capacity Relationship

A relationship between the oxalate-extractable Al and Fe content and the maximum adsorption capacity would be convenient and beneficial as it could eliminate time consuming isotherm testing. The Al_{ox} content (80:1 solution to WTRS) and Q_{max} of the Al-based WTRS had a good correlation ($R^2 = 0.78$) as shown in Figure 4.22. At the same mass quantity Al-based WTRS had approximately 4 times the capacity for P adsorption than Fe-based WTRS (Figure 4.22). There was not enough data to demonstrate a relationship between Fe-based WTRS and Q_{max}. It would be beneficial to observe if a relationship of Fe_{ox} and Q_{max} exists for Fe-based WTRS and a wider range in Al and Fe content of the WTRS samples would better describe the Al_{ox}/Fe_{ox} and Q_{max} relationship. However, without further data the relationship is restricted to the results of this study. Caution must be exercised in using the derived relationship since other effects such as pH, particle size, and age are not taken into account.

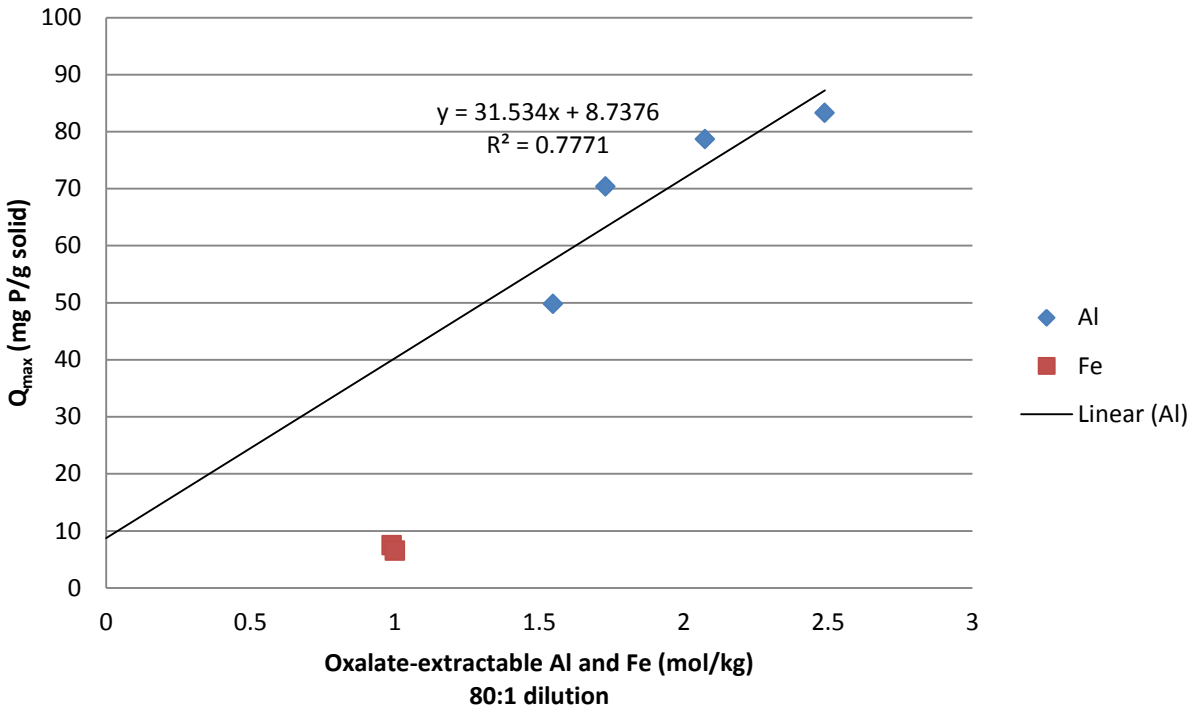

Figure 4.22 Relationship between Langmuir maximum phosphorus adsorption capacity (Q_{max}) and acid ammonium oxalate-extractable aluminum (Al_{ox}, 80:1 solution to WTRS ratio)

4.6 Phosphorus Removal by Batch Treatment of Municipal Primary Wastewater Effluent Using WTRS

Water treatment residual solids performed well when adsorbing phosphate from municipal primary wastewater effluent in batch treatment. The WTRS removed P within acceptable ranges of their target final P concentration. The effects of re-suspending the settled WTRS were observed since the WTRS may not have used their full P capacity before they settled. Also, settled WTRS would only have one surface exposed and available for P adsorption if not already covered by other settled material. Therefore the settled WTRS may have additional capacity for P adsorption. Re-suspending the settled WTRS after an initial equilibrium had little effect on the removal of P except in the case of the Saskatoon WTRS. Phosphate adsorption in batch treatment of municipal primary wastewater effluent results can be found in Appendix D.

4.6.1 Saskatoon WTRS Batch Treatment Tests

The Saskatoon WTRS were able to remove significant amounts of P (Figure 4.23). The majority of P was removed within the initial 5 days. The final total P concentrations for the objective based, half, and exceeding WTRS dosages were 0.74, 1.85, and < 0.05 mg P/L respectively. The objective based WTRS dosage was within 3.0% of its target final P concentration of 0.5 mg P/L. The exceeding WTRS dosage removed P to less than detection limits within the first day surpassing its target final concentration of 0.1 mg P/L. The final P concentration the half dosage achieved was 1.85 mg P/L which was 2.5 times that of the objective based dosage final P concentration.

Re-suspending the settled WTRS (Day 15) had a significant impact on the adsorption of P removing an additional 7.1% and 80.6% P with the objective based and half WTRS dosages respectively. The remixing of the Saskatoon half WTRS dosage had a much larger impact than the remixing of the alum based WTRS from Prince Albert and Buffalo Pound which had negligible effect. Collision and breaking up (slaking) of the WTRS may increase the surface area available for P adsorption and may be a source of variability (Dayton and Basta 2005a). The Saskatoon Fe dominated WTRS may have collided and broken up during remixing thereby increasing the surface area for P adsorption in comparison to Al dominated WTRS.

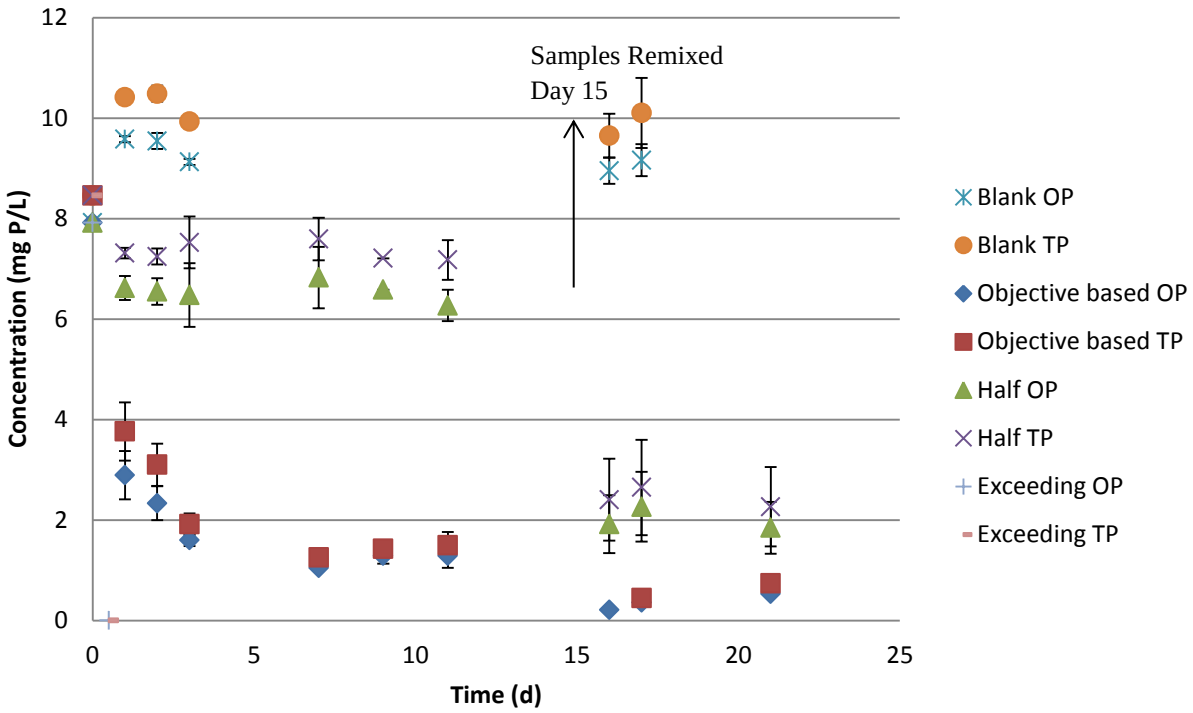

Figure 4.23 Phosphorus removal by batch treatment of municipal primary wastewater effluent using Sample 1 Saskatoon ferric sulphate WTRS (error bars represent standard deviation of replicate results)

The turbidity decreased with time and was unaffected by re-suspension (Figure 4.24) due to the flocculation of material by the WTRS coagulant. The majority of turbidity was removed in the initial 5 days which corresponds with the initial fast P removal suggesting that the WTRS had settled quickly and had reduced P removal once settled.

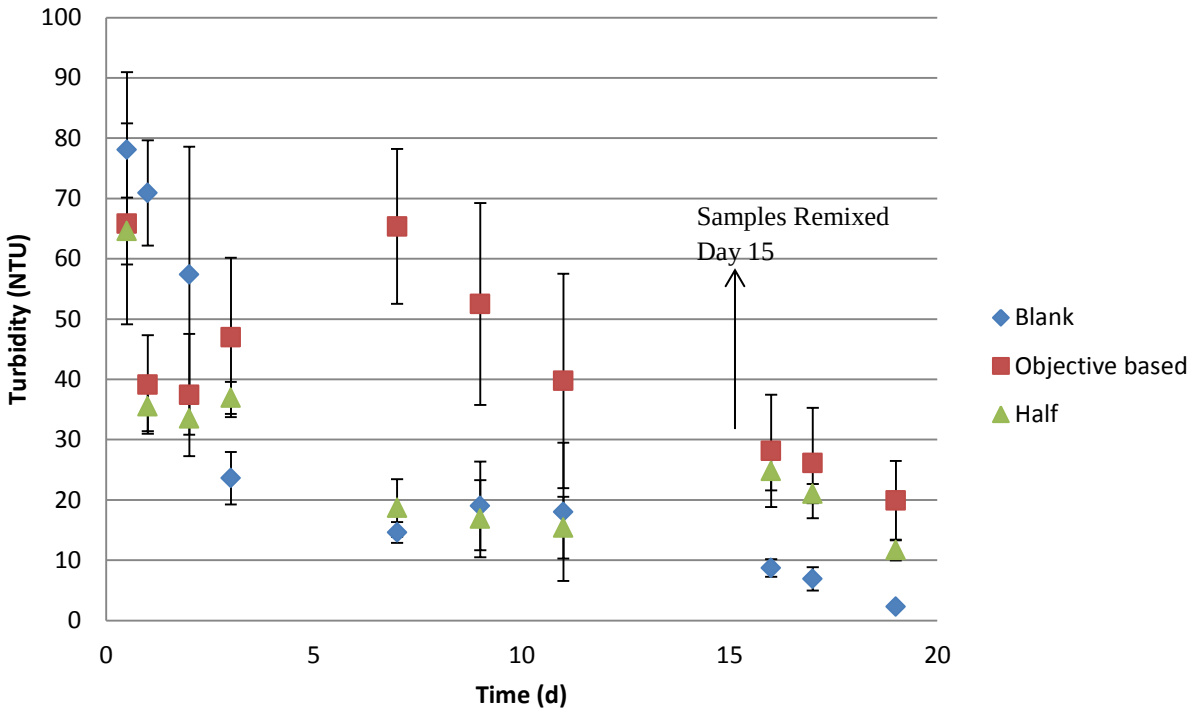

Figure 4.24 Turbidity of municipal primary wastewater effluent treated with Sample 1 Saskatoon ferric sulphate WTRS (error bars represent standard deviation of replicate results)

4.6.2 Prince Albert WTRS Batch Treatment Tests

The Prince Albert WTRS were able to remove significant amounts of P (Figure 4.25). The majority of P was removed within the initial 5-10 days. The final total P concentrations for the objective based, half, and exceeding WTRS dosages were 0.91, 5.29, and 0.16 mg P/L respectively. The objective based WTRS dosage was within 5.2% of its target final P concentration of 0.5 mg P/L. The exceeding WTRS dosage achieved a final total P concentration within 1.3% of its target of 0.05 mg P/L. The final total P concentration of the half dosage was 5.29 mg P/L which was about 6 times that of the objective based dosage final total P concentration. Re-suspending the settled WTRS (Day 28, 20, and 15) had little effect removing an additional 11, 2.2, and 2.8% P for the objective based, half, and exceeding dosages respectively.

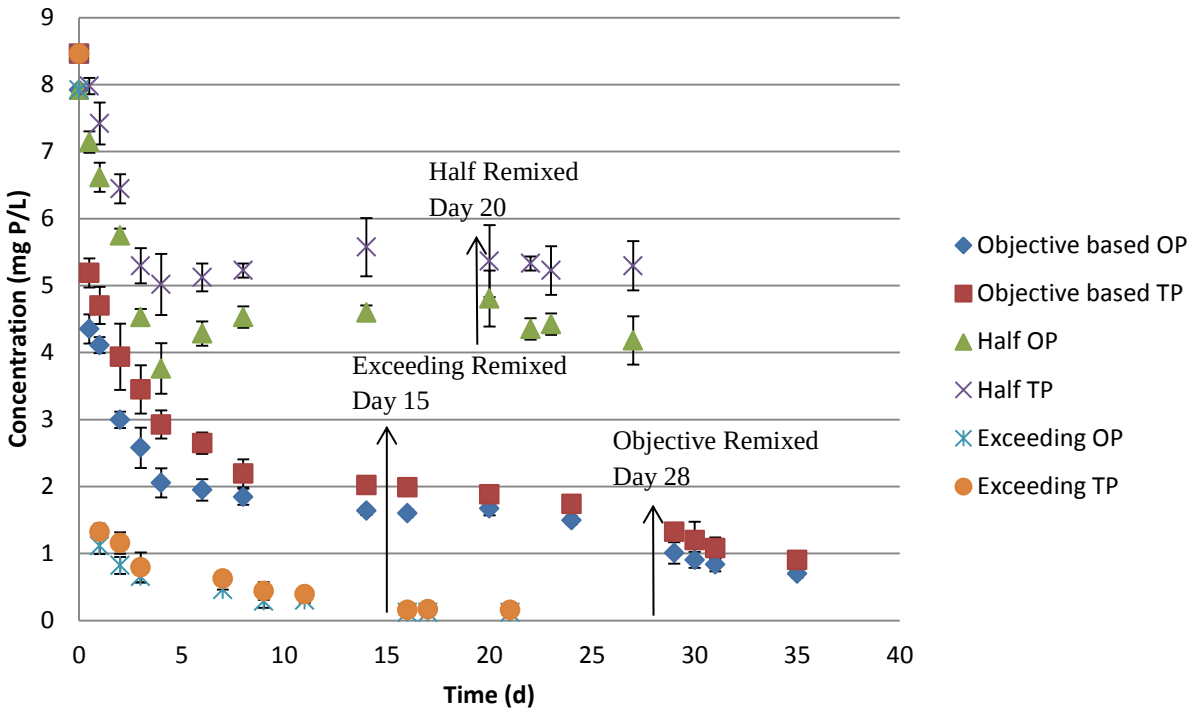

Figure 4.25 Phosphorus removal by batch treatment of municipal primary wastewater effluent using Sample 1 Prince Albert alum WTRS (error bars represent standard deviation of replicate results)

The turbidity decreased with time and was unaffected by re-suspension (Figure 4.26) due to the flocculation of material by the WTRS coagulant. The majority of turbidity was removed in the initial 5-10 days which corresponds with the initial fast P removal suggesting that the WTRS had settled quickly and had reduced P removal once settled.

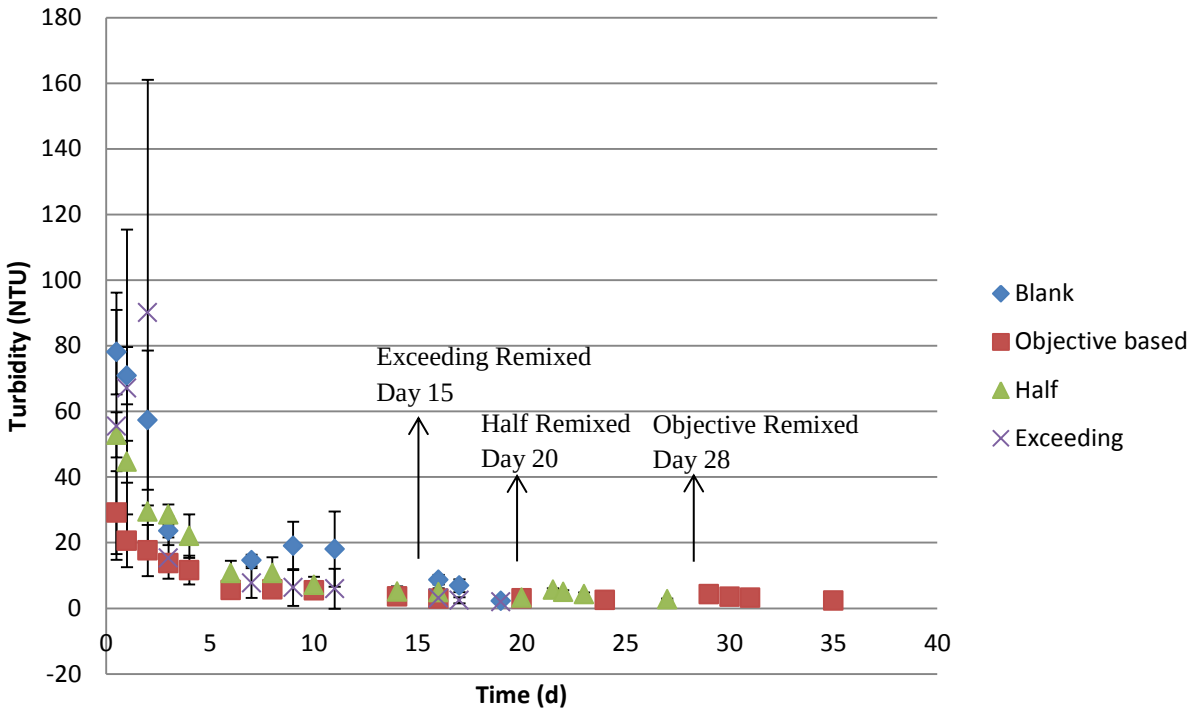

Figure 4.26 Turbidity of municipal primary wastewater effluent treated with Sample 1 Prince Albert alum WTRS (error bars represent standard deviation of replicate results)

4.6.3 Buffalo Pound WTRS Batch Treatment Tests

The Buffalo Pound WTRS were able to remove significant amounts of P (Figure 4.27). The majority of P was removed within the initial 5-10 days. The final total P concentrations for the objective based, half, and exceeding WTRS dosages were 1.01, 4.91, and 0.20 mg P/L respectively. The objective based WTRS dosage was within 6.4% of its target final P concentration of 0.5 mg P/L. The exceeding dosage achieved a final total P concentration within 5.8% of its target final concentration of 0.05 mg P/L. The final total P concentration of the half dosage was 4.91 mg P/L which was about 5 times that of the objective based dosage final total P concentration. Re-suspending the settled WTRS (Day 28, 20, and 15) had little effect removing an additional 7.5, 2.0, and 5.8% P for the objective based, half, and exceeding dosages respectively.

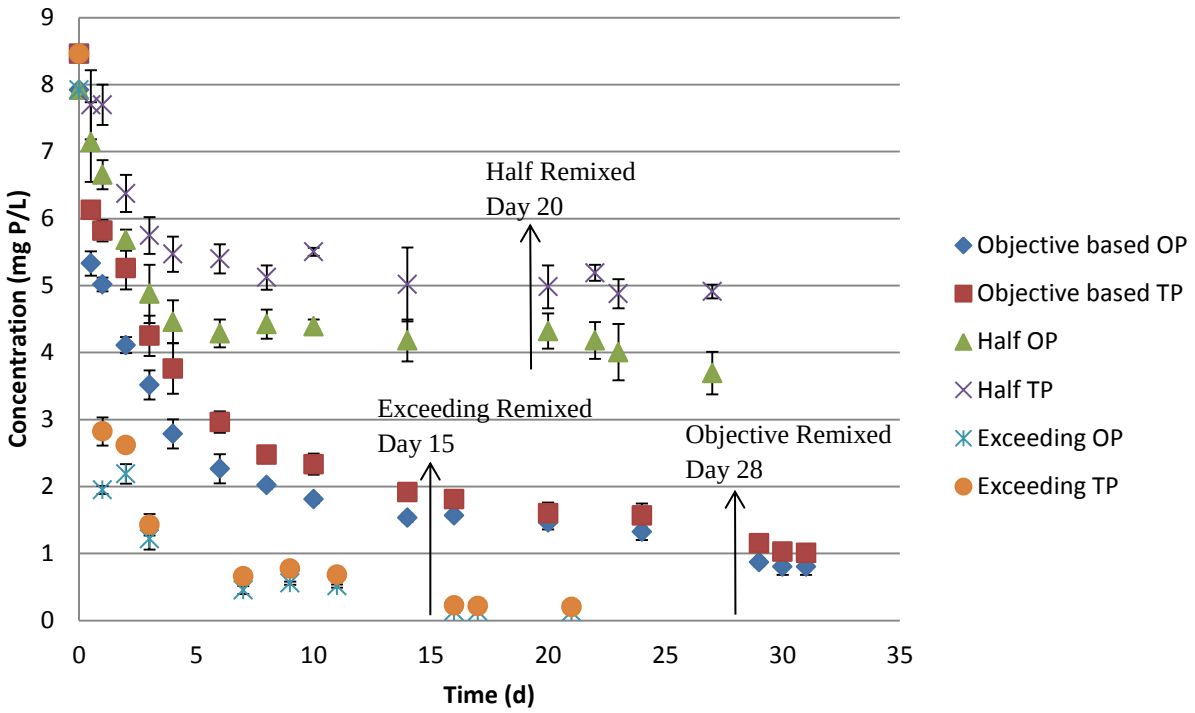

Figure 4.27 Phosphorus removal by batch treatment of municipal primary wastewater effluent using Sample 1 Buffalo Pound alum WTRS (error bars represent standard deviation of replicate results)

The turbidity decreased with time and was unaffected by re-suspension (Figure 4.28) due to the flocculation of material by the WTRS coagulant. The majority of turbidity was removed in the initial 5-10 days which corresponds with the initial fast P removal suggesting that the WTRS had settled quickly and had reduced P removal once settled.

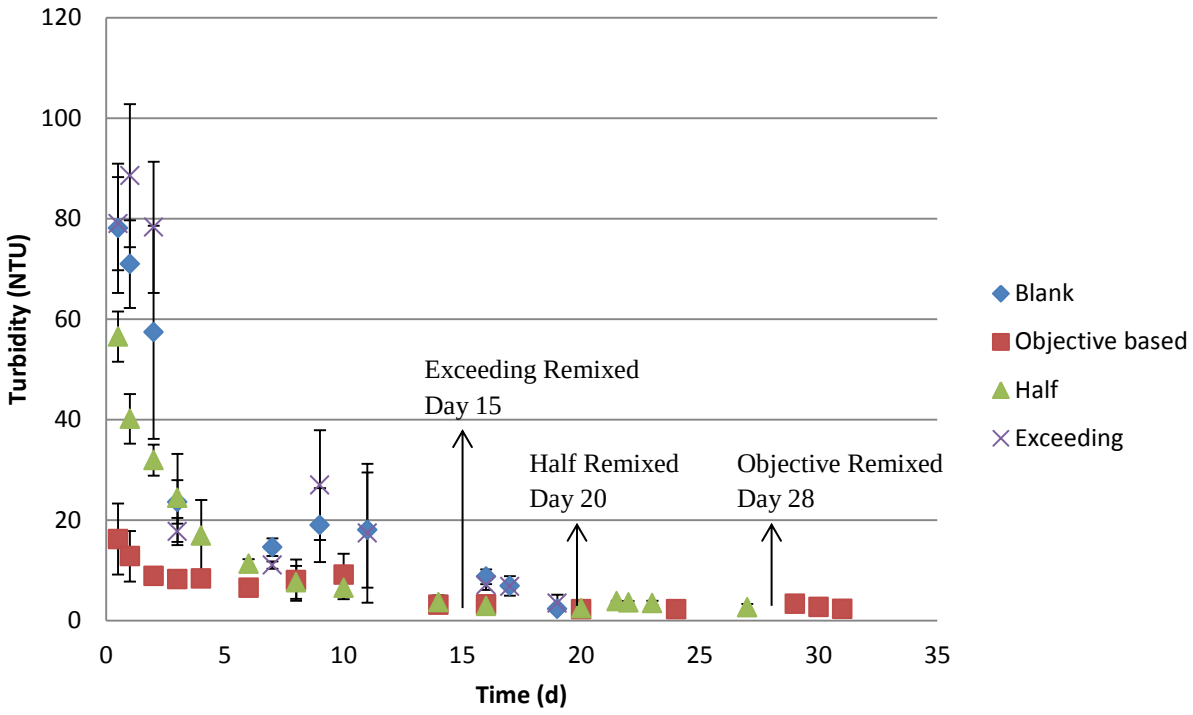

Figure 4.28 Turbidity of municipal primary wastewater effluent treated with Sample 1 Buffalo Pound WTRS (error bars represent standard deviation of replicate results)

4.6.4 Summary of Phosphorus Removal by Batch Treatment of Municipal Primary Wastewater Effluent Using WTRS

A summary of the P removal batch treatment results for municipal primary wastewater effluent using WTRS is presented in Table 4.7. The pH of the wastewater throughout treatment ranged between 8.3-8.7 which was similar to the blank wastewater sample suggesting the WTRS have negligible effect on pH at these WTRS dosages. When treating municipal primary wastewater effluent the majority of P was removed within the initial 5-10 days. Initial fast phosphorus sorption kinetics are due to reaction with surface sites then sorption slows down due to slow P diffusion into pores (Babatunde and Zhao 2010; Makris et al. 2005a,b; Novak and Watts 2005; Lookman et al. 1995). Neither the objective based nor the exceeding dosage for all WTRS achieved their theoretical final P concentrations. However, they were all within 6.4% of their target final P concentrations. This was likely due to competitive species in the wastewater interfering with P adsorption. Re-suspending the settled WTRS appeared to have greater impact on the objective based WTRS dosages while having a negligible effect on the half (excluding

Saskatoon WTRS) and exceeding dosages ability to remove P. The negligible impact of re-suspending was likely due to the coagulants of the WTRS having flocculated suspended material therefore the period of time that the particles remained in suspension once remixed was short. The fast initial turbidity decrease for all WTRS coincided with the fast initial P removal suggesting the WTRS settled quickly and were less effective once settled.

The half and exceeding dosages suggest that the impacts of proper doses are important. The objective based dosages for Prince Albert and Buffalo Pound WTRS removed 2.1-2.4 times as much P as their respective half dosages. This suggests for the alum residuals that the half dosages would remove less than 50% than the desired dosage. The objective based dosage for the iron WTRS (Saskatoon) removed 1.2 times as much as the half dosage which suggests that inaccurate dosing of iron WTRS may still achieve acceptable P removal. However, the Saskatoon WTRS may have broken apart during remixing thereby increasing surface area and P adsorption. The exceeding dosages for all WTRS removed approximately 98-100% of P compared to the objective based dosages removing 88-91% P. However, the exceeding dosage took more than 3 times the amount of WTRS to achieve an additional 10% of P removal. This confirms a non-linear relationship between the WTRS dose and the P removal capability.

Table 4.7 Summary of phosphorus removal by batch treatment of municipal primary wastewater effluent using WTRS

Dose	Pre-Re-suspension C_e (mg P/L)			Final C_e (mg P/L)		
	SK	PA	BP	SK	PA	BP
Objective based	1.29	1.74	1.57	0.74	0.91	1.01
Half	7.18	5.36	4.98	1.85	5.29	4.91
Exceeding	< 0.05	0.39	0.68	< 0.05	0.16	0.20

4.7 Phosphorus Removal by Batch Treatment of Agricultural Runoff Water Using WTRS

Phosphorus removal treatment of agricultural runoff water was not efficient (Figure 4.29) (see Appendix E for results of individual replicate tests and statistical analysis of replicates). The target final total P concentration for the WTRS was 0.5 mg P/L. The alum and iron residuals performed similarly. The Saskatoon orthophosphate triplicates were not statistically similar. The agricultural pond water established a relatively consistent P concentration at approximately 2.5 mg P/L. It was remixed which had no effect as the P concentration remained the same (Day 7 to Day 8). The negligible impact of re-suspending was likely due to the coagulants of the WTRS having flocculated suspended material, as suggested by the turbidity (Figure 4.30), therefore the period of time that the particles remained in suspension once remixed was short. Interfering compounds and blockages of adsorption sites may also be a factor. The dosage of WTRS was doubled and the water remixed on Day 13. The additional WTRS dosage was expected to have a significant impact on the P concentration. However, the final concentration was only approximately 1.6 mg P/L.

The orthophosphate concentration of the agricultural pond water was 1.92 mg P/L of the 2.86 mg P/L total phosphorus. This was approximately 67% compared to the 94% orthophosphate of the municipal primary wastewater effluent. The adsorption of P from the agricultural runoff water may have been ineffective due to other forms of phosphorus that were not readily adsorbed. Conflicting species of ions present in the agricultural pond water may also have interfered with the WTRS ability to adsorb P. Further research should include a chemical analysis of the agricultural runoff water.

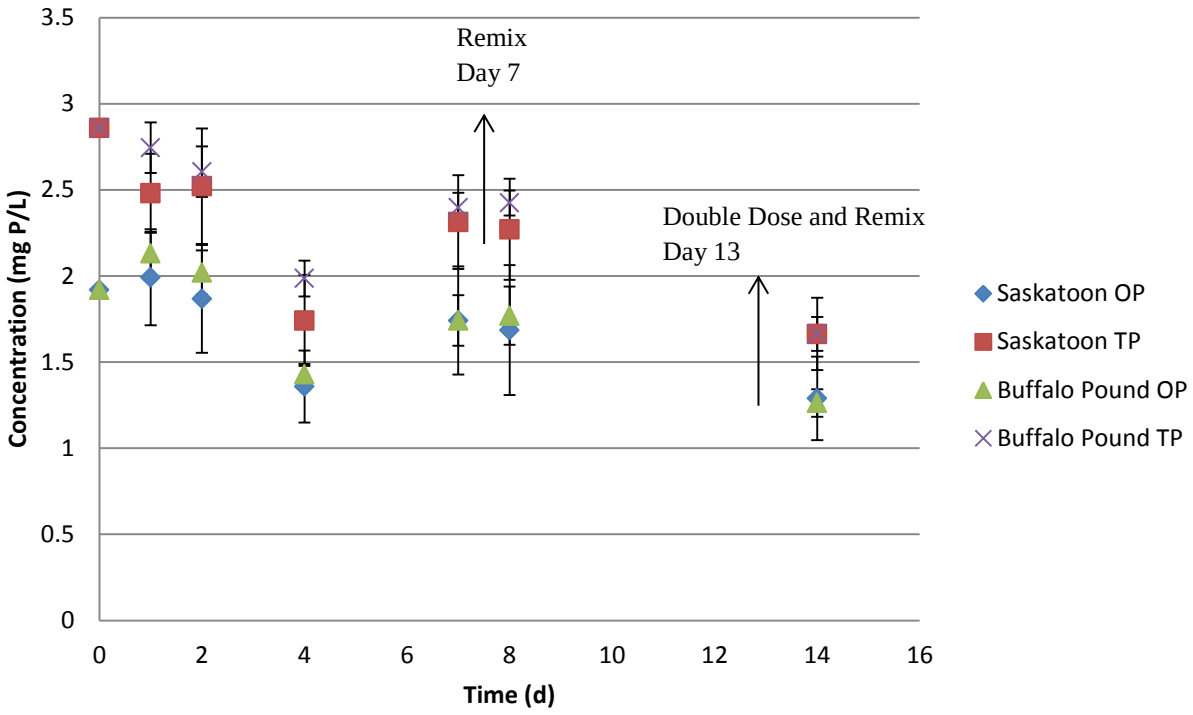

Figure 4.29 Phosphorus removal by batch treatment of agricultural runoff water using Al- and Fe-based WTRS (error bars represent standard deviation of replicate results)

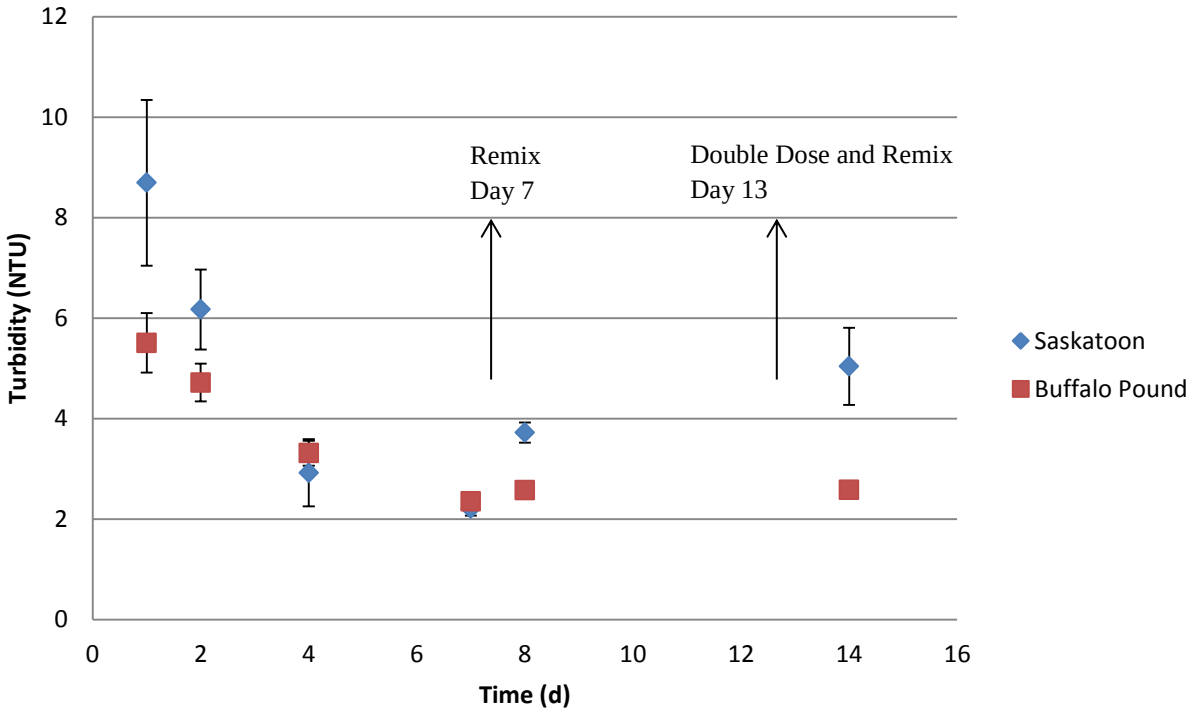

Figure 4.30 Turbidity of agricultural runoff water treated with Al- and Fe-based WTRS (error bars represent standard deviation of replicate results)

4.8 Desorption of Phosphorus from WTRS

Desorption of P from WTRS was minimal (Table 4.8) (see Appendix F for detailed desorption results). Typically, desorption was ≤ 2% which is consistent with other studies (Dayton and Basta 2005a; Makris et al. 2005a; Makris et al. 2004). The minimal desorption is also consistent with Langmuir adsorption isotherm behaviour that indicates chemisorption is the primary mechanism which involves strong bonds between the adsorbate and adsorbent (Oura et al. 2003; Luth 1993). Further the low percentage desorption could be due to phosphate molecules bound in micropores (< 1.5 nm) which would likely only desorb when increasing amounts of activation energy are supplied to overcome energetic barriers associated with micropores (Makris et al. 2004). The alum residual half dosages had higher desorption of P ranging from 7.81 to 10.6%. This may be related to the low amount of P adsorbed by the alum residual half dosages. Makris et al. (2005a) found an inverse trend in the percentage of sorbed and desorbed P. It is apparent that desorption of P off WTRS was low.

Table 4.8 Phosphorus desorption from alum and ferric WTRS

WTRS and Dosage Level	P Sorbed (mg)	P Desorbed (mg)	% Desorbed
Saskatoon (Fe)			
Objective based	46.3	0.87	1.87
Half	37.2	0.76	1.97
Exceeding	50.8	0.25	0.49
Prince Albert (Al)			
Objective based	45.3	0.76	1.67
Half	19.0	1.49	7.81
Exceeding	49.8	< 0.05	< 0.10
Buffalo Pound (Al)			
Objective based	44.7	0.11	0.25
Half	21.3	2.25	10.6
Exceeding	49.6	< 0.05	< 0.10

4.9 Application of Water Treatment Residual Solids for Phosphorus Removal Treatment of Lagoons and Stormwater Retention Ponds

Water treatment residual solids have been shown to be effective at adsorbing phosphorus. Compared to other low-cost P adsorbents they have high potential for practical application (Table 4.9). Other benefits are that the waste material would be recycled and would have minimal monetary costs to acquire from water treatment plants.

Table 4.9 Phosphorus adsorption capacities of Al and Fe WTRS and several P adsorbents reported in the literature

Adsorbent	Maximum Adsorption Capacity Q_{max} (mg P/g solid)	Reference
Alum WTRS	53.5-82.0	This research
Ferric sulphate WTRS	6.41-7.37	This research
Activated alumina	17.5	Shin et al. 2004
Al10SBA-15	26.7	Shin et al. 2004
Blast furnace slag	44.2	Sakadevan and Bavor 1998
Ferrihydrite	42.78	Borggaard et al. 2005
Ferrihydrite-modified diatomite	37.3	Xiong 2009
Fly ash	0.86	Drizo et al. 1999
Goethite	6.42, 16.4	Borggaard et al. 2005; Oh et al. 1999
Hematite	2.2	Oh et al. 1999
Iron-hydroxide eggshell	4.73	Mezenner et al. 2009
Limestone	0.68	Drizo et al. 1999
Red mud with HCl treatment	0.58	Huang et al. 2008
Sand	0.129	Arias et al. 2001
Steel slag	5.3	Xiong et al. 2008
Synthesized aluminum oxide	35.03	Borggaard et al. 2005
Synthesized iron oxide coated sand	0.49	Boujelben et al. 2008
Zeolite	0.46, 2.15	Drizo et al. 1999; Sakadevan and Bavor 1998

An application of the WTRS would be to apply it to wastewater lagoons or stormwater retention ponds to reduce the phosphorus content. It would be a batch application to remove phosphorus prior to discharge of the lagoon in the spring or fall. The material could be applied by motorboat which would provide rapid even distribution of the WTRS and adequate mixing. Another feasible method would be spraying the material onto the water source from a tanker. This method

would require the tanker to be able to drive around the lagoon or stormwater retention pond to achieve even distribution as well as a motorboat to drive around the water source to provide turbulence and mixing.

Other methods of application include a mechanical pumping continuous injection system into the lagoon inlet sewer. The injection system would be built with the lagoon and would require higher initial capital costs and operation and maintenance costs. These application methods are often used for applying coagulants such as alum to lagoons (Graham and Hunsinger n.d.) The WTRS would settle to the bottom of the lagoon and become part of the sludge layer and be removed by desludging of the lagoon. Graham and Hunsinger (n.d.) found that alum treatments of lagoons with dosages of approximately 150 mg/L to reduce effluent total phosphorus to typically < 1 mg/L contributed 0.75 to 1.0 cm deposition per treatment. An example application of WTRS to a lagoon and stormwater retention pond is given in Table 4.10 and Table 4.11, respectively.

Table 4.10 Example of WTRS application to remove phosphorus from a wastewater lagoon

Saskatoon WWTP Effluent Discharge in 2011[a]	29.7 million cubic meters
Population of Saskatoon in 2011[b]	222189
Population of Town with Lagoon	1000
% of Saskatoon Population	0.45
Town Wastewater Yearly Effluent Discharge	0.134 million cubic meters
WTRS Treatment Period	≈180 days (Spring/Fall discharge)
Lagoon Wastewater to be Treated with WTRS	0.067 million cubic meters
Phosphorus Concentration of Lagoon[c]	3 mg/L
Target Phosphorus Concentration in Effluent[d]	1 mg/L
Phosphorus Removed	133669984 mg P
Maximum Adsorption Capacity of WTRS, Q_{max}	
Saskatoon	7.37 mg P/g WTRS
Prince Albert	53.5 mg P/g WTRS
Buffalo Pound	78.1 mg P/g WTRS
Adsorption Capacity of WTRS, Q[e]	
Saskatoon	5.01 mg P/g WTRS
Prince Albert	45.7 mg P/g WTRS
Buffalo Pound	71.4 mg P/g WTRS
WTRS Mass Required[f]	
Saskatoon	26667162 g
Prince Albert	2927373 g
Buffalo Pound	1871380 g
WTRS Volume Required (Assume 10% Solids)	
Saskatoon	266672 L
Prince Albert	29274 L
Buffalo Pound	18714 L
Number of 30 Metric Tonne Trucks Required	
Saskatoon	9 (8.89 rounded up)
Prince Albert	1 (0.98 rounded up)
Buffalo Pound	1 (0.62 rounded up)
Man-hours Required for Application[g]	132

a City of Saskatoon 2011
b Statistics Canada 2012
c Chapter 2 Table 5
d Saskatchewan Ministry of Environment 2008
e Sample 1 Langmuir linearization equations
f Chapter 3 Equation 1 and Sample 1 Langmuir linearization equation
g 1.5 man-hours per million gallons (Graham and Hunsinger n.d.)

Table 4.11 Example of WTRS application to remove phosphorus from a stormwater retention pond

Permanent Pool Depth[a]	1.5 m
Length to Width Ratio[a]	4:1
Side Slopes of Permanent Pool[a]	5:1
Width	100 m
Length	400 m
Side Slope Height	1.5 m
Side Slope Width	0.3 m
Volume of Stormwater Pond	60270 cubic meters
Phosphorus Concentration of Stormwater Pond	2 mg/L
Target Phosphorus Concentration[b]	1 mg/L
Phosphorus Removed	60270000 mg P
Maximum Adsorption Capacity of WTRS, Q_{max}	
Saskatoon	7.37 mg P/g WTRS
Prince Albert	53.5 mg P/g WTRS
Buffalo Pound	78.1 mg P/g WTRS
Adsorption Capacity of WTRS, Q[c]	
Saskatoon	5.01 mg P/g WTRS
Prince Albert	45.7 mg P/g WTRS
Buffalo Pound	71.4 mg P/g WTRS
WTRS Mass Required[d]	
Saskatoon	12023865 g
Prince Albert	1319913 g
Buffalo Pound	843780 g
WTRS Volume Required (Assume 10% Solids)	
Saskatoon	120239 L
Prince Albert	13199 L
Buffalo Pound	8438 L
Number of 30 Metric Tonne Trucks Required	
Saskatoon	4 (4.00 rounded up)
Prince Albert	1 (0.44 rounded up)
Buffalo Pound	1 (0.28 rounded up)
Man-hours Required for Application[e]	23.9

a Saskatchewan Environment 2006b
b Saskatchewan Ministry of Environment 2008
c Sample 1 Langmuir linearization equations
d Chapter 3 Equation 1 and Sample 1 Langmuir linearization equation
e 1.5 man-hours per million gallons (Graham and Hunsinger n.d.)

The example application calculations were done using approximate but typical values. The application of the WTRS was highly dependent on the volume of water to be treated, the initial and target final phosphorus concentrations (i.e. the amount of phosphorus to be removed), and the water content of the water treatment residual solids. A lower initial P concentration and lower water content of the WTRS would significantly reduce the total volume of WTRS sludge required. The water content was assumed to be 90% of the unaltered WTRS sludge but it would be beneficial and practical to remove water (e.g. decant) without impacting the WTRS. Gravity thickeners would be the optimal location to collect WTRS to achieve the highest percent solids without producing cake. The goal of the application is to be able to use the WTRS without having to perform any preparatory actions such as breaking apart cake or sieving particles to obtain a preferred particle size. It would be safer to dose a higher volume of WTRS sludge since it required many days and re-suspending to finally achieve the target final P concentration. Since the majority of P is removed in the early stages of treatment, a higher dosage would improve the likelihood of achieving the target final P concentration in a faster period of time while also offering a buffer to alleviate interferences by competitive species.

CHAPTER 5 Conclusions and Recommendations

5.1 Conclusions

The primary objective of this research was to investigate the use of water treatment residual solids (WTRS) for immobilization of soluble phosphorus and prevention of phosphorus movement to the environment within effluents from wastewater lagoons and stormwater retention ponds. The following are conclusions from this research:

1. Aluminum and iron based WTRS each had the capability to remove P from the water column. The experiment results indicate aluminum based WTRS were more effective than iron based WTRS at adsorbing phosphorus from phosphate-spiked deionized water. The majority of phosphorus was removed during the initial 2-3 days.

2. The Langmuir isotherm was an accurate model of the phosphorus adsorption behaviour of WTRS (R^2 = 0.97-1.00 linearized transformed data). The Freundlich isotherm was not as good a model of phosphorus adsorption behaviour of WTRS (R^2 = 0.63-0.87 linearized transformed data). The Langmuir isotherm model provided an excellent fit to both the aluminum based and iron based WTRS adsorption behaviour. The iron based WTRS adsorption behaviour had a more consistent fit to the Freundlich isotherm model than the aluminum based WTRS adsorption behaviour.

3. The Al based WTRS Q_{max} values obtained in this study ranged from 53.5 to 82.0 mg P/g solid. The iron based WTRS Q_{max} values obtained in this study ranged from 6.41 to 7.37 mg P/g solid.

4. The aluminum based WTRS had much higher capacities for phosphorus adsorption compared to the iron based residuals. The iron based residuals contained approximately equivalent, if not more, iron mass per unit mass of residual solid than the aluminum based residuals contained aluminum mass per unit mass of residual solid yet had approximately 7 to 13 times smaller phosphorus capacities. However, in terms of moles

of coagulant metal species (Al or Fe) per unit mass of residual solid, the ferric based residuals did contain less than the aluminum based residuals.

5. WTRS collected during the summer and fall produced negligible differences in phosphorus adsorption abilities. The indication is seasonal variations in the WTRS P adsorption capacity are minor during that portion of the year.

6. The calcium content of the WTRS contributed little to the removal of phosphorus from phosphate-spiked deionized water, municipal primary wastewater effluent, and agricultural runoff water.

7. There is an indication a relationship exists between Q_{max} and Al_{ox} content based on limited data. Further data is required to confirm the relationship. There is insufficient data available in this research to conclusively quantify the relationship.

8. Aluminum and iron based WTRS each had the capability to remove P from municipal primary wastewater effluent. From the results aluminum based WTRS were more effective than iron based WTRS at adsorbing phosphorus from municipal primary wastewater effluent in batch adsorption treatment. The objective and exceeding WTRS dosages removed phosphorus to within 6.4% of their target final P concentrations (1.0 and 0.5 mg P/L respectively). The majority of phosphorus was removed during the initial 5-10 days from the municipal primary wastewater effluent.

9. The aluminum and iron based WTRS were not effective at adsorbing phosphorus from agricultural runoff water. After remixing the settled WTRS and doubling the dosage the WTRS only removed approximately 20-25% phosphorus. This may have been due to the total phosphorus being only 67% orthophosphate whereas the municipal primary wastewater effluent total phosphorus was 94% orthophosphate. Interfering compounds and blockages of adsorption sites may also be a factor.

10. Re-suspension and resettling of WTRS after an initial cycle of P adsorption and settling had negligible effect upon the P concentration in the water column. This may suggest that the WTRS phosphorus capacity was filled prior to the residuals being completely settled or that WTRS ability to adsorb phosphorus was not significantly affected by being settled. The WTRS may also have caused flocculation in the wastewater and did not remain suspended for any significant period once re-suspended, as shown by the turbidity.

11. WTRS had negligible effect on the pH of the wastewater solutions at the dosed concentrations.

12. Control of WTRS dosage was shown to be important. The half dosage typically removed slightly less than half of the phosphorus that the objective based dosage removed. The exceeding dosages removed approximately an additional 10% of phosphorus compared to the desired dosage however it required approximately 3 times as much WTRS dry mass.

13. Short term (14 days) desorption of phosphorus from WTRS utilized in P adsorption tests was low, typically less than 2% and reaching as high as 10.6% of the total P adsorbed.

14. The application of Al-based WTRS would be more practical than Fe-based WTRS. A large mass of Fe-based WTRS would be required due to the low phosphorus adsorption capacity of the Fe-based WTRS. To reduce the volume of WTRS slurry required for application the slurry should be collected from a point in the water treatment process where the percent solids are highest such as a gravity thickener.

5.2 Recommendations

The following recommendations outline areas to explore in future studies of WTRS to better understand their characteristics and applicability for phosphorus removal treatment:

1. For comparative purposes it would be beneficial to have a standardized isotherm testing procedure. The properties of WTRS vary from all WTPs however standard testing parameters such as pH, temperature, initial P concentrations, particle size (if dried WTRS filter cake, crushing, and sieving are utilized), and equilibrium time (to ensure it is set long enough) should be established for all isotherm tests. If specific testing parameters and conditions can be specified then isotherm results would be more comparative.

2. An investigation of the environmental impact of applying WTRS to lagoons and stormwater retention ponds should be performed. This would involve investigating the pollutants of WTRS (e.g. aluminum toxicity, microbial, pH), their effects within lagoons and stormwater retention ponds, and the treatment systems ability to remove or negate environmental impacts if WTRS are dosed in hazardous concentration ranges.

3. The adsorption of phosphorus by WTRS should be evaluated under various testing conditions. Various conditions could include pH, redox, and temperature (spring/fall).

4. Physical analysis of the WTRS, such as mercury porosimetry and scanning electron microscope imaging to observe the porous structure of the WTRS and particle size distribution analysis, should be performed to identify physical differences between WTRS and their impact on phosphorus adsorption.

5. It appeared that competitive species in the municipal primary wastewater effluent had little impact on the ability of the WTRS to adsorb P. However, batch tests of the wastewater to be treated by WTRS should be performed prior to application to observe the WTRS adsorption behaviour of P and if there are any competitive species in the wastewater.

6. A chemical analysis of the agricultural runoff pond water should be performed to identify the type of P compounds present and other competitive species that may have significantly interfered with phosphorus adsorption by WTRS.

7. Pilot testing of WTRS should be performed in order to evaluate their performance in realistic conditions where they would be exposed to various environmental conditions. WTRS are unique to each WTP and the specific time collected therefore adsorption isotherms would need to be produced prior to application to determine appropriate dosing requirements.

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APPENDIX A

Isotherm Model Descriptions

Brunauer-Emmett-Teller

The Brunauer-Emmett-Teller (BET) isotherm can be used to determine multilayer adsorption behaviour, monolayer adsorption capacity, and heat of adsorption at various adsorption layers (Ebadi et al. 2009). The BET equation was originally developed for gas phase adsorption and is defined by (Ebadi et al 2009):

$$\frac{Q}{Q_m} = \frac{cx}{(1-x)(1-x+cx)} \qquad [A.1]$$

where Q is the adsorption density (mg P g^{-1}), Q_m (mg P g^{-1}) and c are BET parameters which can be found by linear regression analysis of experimental adsorption data, and x is the ratio of the partial pressure of the adsorbate to its saturation partial pressure at the system temperature ($x = P/P^S$).

When applying the BET equation to liquid phase adsorption the liquid phase concentration, C replaces the partial pressure of the adsorbate, P (Ebadi et al. 2009). Many researchers use the saturation concentration of the adsorbate in liquid phase, C_S instead of P^S however this may not be the correct approach (Ebadi et al. 2009). As the BET isotherm was developed for gas phase adsorption, it may not directly apply to liquid phase adsorption without adjusting the original equation.

Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich isotherm assumes that there is a surface area where the adsorption energy is homogeneous (Zhao et al. 2007; Kundu and Gupta 2006). It is defined by (Babatunde and Zhao 2010):

$$Q = Q_m e^{-k\varepsilon^2} \qquad [A.2]$$

where Q is the adsorption density (mg P g^{-1}), ε (kJ mol^{-1}) is the Polanyi potential, Q_m (mg P g^{-1}) is the Dubinin-Radushkevich constant, and k (mol^2 kJ^{-2}) is related to the mean free energy of sorption per mole of the sorbate when it is transferred to the surface of the solid from infinity (Kundu and Gupta 2006).

The linearized form of the Dubinin-Radushkevich equation is presented by:

$$\ln Q = \ln Q_m - k\varepsilon^2 \qquad [A.3]$$

Frumkin Isotherm

The Frumkin isotherm deals with lateral interactions among adsorbed species (Bockris and Reddy 1998). It is defined by (Bockris and Reddy 1998):

$$\frac{\theta}{1-\theta} e^{-2a\theta} = KC_e \qquad [A.4]$$

where C_e is the equilibrium concentration in the liquid phase (mg P L^{-1}), K is the adsorption constant, *a* is the interaction coefficient, and θ is equal to [adsorbate on surface sites]/[maximum concentration of surface sites].

The linearized form of the Frumkin equation is presented by:

$$\log\left[\left(\frac{\theta}{1-\theta}\right)\frac{1}{C_e}\right] = \log K + 2a\theta \qquad [A.5]$$

The interactions among adsorbed moles are considered in term *a* where a positive value means attraction between the adsorbed particles and a negative value means repulsion between the molecules (Stumm and Morgan 1995; Bockris and Reddy 1998). When there are no interactions (term *a* is equal to zero) then the Frumkin isotherm reduces to the Langmuir isotherm (Stumm and Morgan 1995; Bockris and Reddy 1998).

Harkins-Jura Isotherm

The Harkins-Jura isotherm accounts for multilayer adsorption and can be explained by a heterogeneous pore distribution (Samarghandi et al. 2009).

The Harkins-Jura isotherm is defined by (Samarghandi et al. 2009):

$$Q = \left(\frac{A}{B_2 + \log C_e}\right)^{0.5} \qquad [A.6]$$

where Q is the adsorption density (mg P g^{-1}), C_e is the equilibrium concentration in the liquid phase (mg P L^{-1}), and A and B are isotherm parameters and constants.

APPENDIX B

WTRS pH and Al, Fe, and Ca Content Data

Table B.1 WTRS pH results

WTRS	Replicate	Sample 1	Average	Sample 2	Average
Saskatoon	1	8.13	8.15	8.22	8.24
	2	8.17		8.25	
Prince Albert	1	7.81	7.81	7.81	7.83
	2	7.81		7.84	
Buffalo Pound	1	6.05	5.98	7.24	7.25
	2	5.91		7.25	

Table B.2 Ammonium oxalate-extractable Al Sample 1 replication 1 results

WTRS	Replicate	Sample Volume (mL)	Total Volume (mL)	AA Spec Al Conc. (mg/L)	Sample Al Conc. (mg/L)	WTRS Al Content (g Al/kg WTRS)	Average WTRS Al Content (g Al/kg WTRS)
Saskatoon	1	5	10	5.0	10	0.80	0.64
	2	5	10	3.0	6	0.48	
Prince Albert	1	5	50	58.5	585	46.8	45.2
	2	5	50	54.5	545	43.6	
Buffalo Pound	1	5	50	71.0	710	56.8	58.4
	2	5	50	75.0	730	58.4	

Table B.3 Ammonium oxalate-extractable Al Sample 1 replication 2 results

WTRS	Sample Volume (mL)	Total Volume (mL)	AA Spec Al Conc. (mg/L)	Sample Al Conc. (mg/L)	WTRS Al Content (g Al/kg WTRS)
Saskatoon	2	10	4.0	20	1.6
Prince Albert	5	50	48.0	480	38.4
Buffalo Pound	5	100	33.5	670	53.6

Table B.4 Ammonium oxalate-extractable Fe Sample 1 replication 1 results

WTRS	Replicate	Sample Volume (mL)	Total Volume (mL)	AA Spec Fe Conc. (mg/L)	Sample Fe Conc. (mg/L)	WTRS Fe Content (g Fe/kg WTRS)	Average WTRS Fe Content (g Fe/kg WTRS)
Saskatoon	1	1	200	3.38	676	54.1	54.4
	2	1	200	3.42	684	54.7	
Prince Albert	1	5	50	1.62	16.2	1.30	1.28
	2	5	50	1.59	15.9	1.27	
Buffalo Pound	1	5	50	0.58	5.8	0.46	0.46
	2	5	50	0.58	5.8	0.46	

Table B.5 Ammonium oxalate-extractable Fe Sample 1 replication 2 results

WTRS	Sample Volume (mL)	Total Volume (mL)	AA Spec Fe Conc. (mg/L)	Sample Fe Conc. (mg/L)	WTRS Fe Content (g Fe/kg WTRS)
Saskatoon	1	200	3.50	700	56.0
Prince Albert	5	50	1.61	16.1	1.29
Buffalo Pound	5	50	0.71	7.1	0.57

Table B.6 Ammonium acetate extractable Ca Sample 1 replication 1 results

WTRS	Sample Volume (mL)	Total Volume (mL)	AA Spec Ca Conc. (mg/L)	Sample Ca Conc. (mg/L)	WTRS Ca Content (g Ca/kg WTRS)
Saskatoon	0.9	90	2.42	242	32.3
Prince Albert	0.9	90	2.73	273	36.4
Buffalo Pound	9	90	4.64	46.4	6.2

Table B.7 Ammonium acetate extractable Ca Sample 1 replication 2 results

WTRS	Sample Volume (mL)	Total Volume (mL)	AA Spec Ca Conc. (mg/L)	Sample Ca Conc. (mg/L)	WTRS Ca Content (g Ca/kg WTRS)
Saskatoon	0.9	90	2.72	272	36.3
Prince Albert	0.9	90	2.99	299	39.9
Buffalo Pound	9	90	4.81	48.1	6.4

Table B.8 Ammonium oxalate-extractable Al Sample 2 replication 1 results

WTRS	Replicate	Sample Volume (mL)	Total Volume (mL)	AA Spec Al Conc. (mg/L)	Sample Al Conc. (mg/L)	WTRS Al Content (g Al/kg WTRS)	Average WTRS Al Content (g Al/kg WTRS)
Saskatoon	1	5	10	6.0	12	0.96	0.92
	2	5	10	5.5	11	0.88	
Prince Albert	1	5	50	61.0	610	48.8	50.2
	2	5	50	64.5	645	51.6	
Buffalo Pound	1	5	50	90.0	900	72.0	72.0
	2	5	50	90.0	900	72.0	

Table B.9 Ammonium oxalate-extractable Al Sample 2 replication 2 results

WTRS	Sample Volume (mL)	Total Volume (mL)	AA Spec Al Conc. (mg/L)	Sample Al Conc. (mg/L)	WTRS Al Content (g Al/kg WTRS)
Saskatoon	2	10	5.0	25	2.0
Prince Albert	5	50	54.0	540	43.2
Buffalo Pound	5	100	39.0	780	62.4

Table B.10 Ammonium oxalate-extractable Fe Sample 2 replication 1 results

WTRS	Replicate	Sample Volume (mL)	Total Volume (mL)	AA Spec Fe Conc. (mg/L)	Sample Fe Conc. (mg/L)	WTRS Fe Content (g Fe/kg WTRS)	Average WTRS Fe Content (g Fe/kg WTRS)
Saskatoon	1	1	200	3.69	738	59.0	59.1
	2	1	200	3.70	740	59.2	
Prince Albert	1	5	50	1.19	11.9	0.95	0.92
	2	5	50	1.12	11.2	0.90	
Buffalo Pound	1	5	50	2.74	27.4	2.19	2.18
	2	5	50	2.72	27.2	2.18	

Table B.11 Ammonium oxalate-extractable Fe Sample 2 replication 2 results

WTRS	Sample Volume (mL)	Total Volume (mL)	AA Spec Fe Conc. (mg/L)	Sample Fe Conc. (mg/L)	WTRS Fe Content (g Fe/kg WTRS)
Saskatoon	1	200	3.28	656	52.5
Prince Albert	5	50	1.30	13.0	1.0
Buffalo Pound	5	50	2.81	28.1	2.3

Table B.12 Ammonium acetate extractable Ca Sample 2 replication 1 results

WTRS	Sample Volume (mL)	Total Volume (mL)	AA Spec Ca Conc. (mg/L)	Sample Ca Conc. (mg/L)	WTRS Ca Content (g Ca/kg WTRS)
Saskatoon	0.9	90	2.64	264	35.2
Prince Albert	0.9	90	2.78	278	37.1
Buffalo Pound	0.9	90	0.93	93.0	12.4

Table B.13 Ammonium acetate extractable Ca Sample 2 replication 2 results

WTRS	Sample Volume (mL)	Total Volume (mL)	AA Spec Ca Conc. (mg/L)	Sample Ca Conc. (mg/L)	WTRS Ca Content (g Ca/kg WTRS)
Saskatoon	0.9	90	2.64	264	35.2
Prince Albert	0.9	90	2.85	285	38.0
Buffalo Pound*	9	90	2.90	29.0	11.6

* WTRS mass of 0.5 g used for Buffalo Pound Ca extraction for replication 2

APPENDIX C

Phosphorus Adsorption in P-Spiked Deionized Water Results

Table C.1 Phosphorus adsorption in P-spiked deionized water using Sample 1 Saskatoon WTRS results

Initial P Concentration, C_o (mg P/L)	Replicate	Equilibrium P Concentration, C_e (mg P/L)	P Adsorbed, C_{ab} (mg P/L)	% Removal	Q (mg P/g WTRS)	C_e/Q (g/L)
2.02	1	0.38	1.64	81.3	3.38	0.11
	2	0.26	1.76	87.0	3.61	0.07
	3	0.29	1.72	85.5	3.55	0.08
2.37	1	0.30	2.07	87.2	4.26	0.07
	2	0.33	2.04	85.9	4.20	0.08
	3	0.28	2.09	88.1	4.30	0.07
	4	0.39	1.99	83.7	4.09	0.09
2.97	1	0.97	1.99	67.2	4.10	0.24
	2	0.90	2.07	69.7	4.26	0.21
	3	0.78	2.18	73.6	4.49	0.17
3.56	1	1.26	2.29	64.5	4.72	0.27
	2	1.18	2.38	66.8	4.90	0.24
	3	1.16	2.40	67.4	4.94	0.23
	4	1.20	2.36	66.2	4.85	0.25
4.74	1	2.10	2.64	55.7	5.44	0.39
	2	2.19	2.55	53.7	5.25	0.42
	3	2.00	2.75	57.9	5.66	0.35
	4	1.96	2.78	58.6	5.72	0.34
5.93	1	2.82	3.11	52.4	6.40	0.44
	2	2.95	2.98	50.2	6.13	0.48
	3	2.72	3.21	54.2	6.62	0.41
	4	2.87	3.06	51.5	6.29	0.46
7.12	1	3.54	3.58	50.3	7.37	0.48
	2	3.81	3.30	46.4	6.80	0.56
	3	3.84	3.28	46.0	6.75	0.57

Table C.2 Phosphorus adsorption in P-spiked deionized water using Sample 2 Saskatoon WTRS results

Initial P Concentration, C_o (mg P/L)	Replicate	Equilibrium P Concentration, C_e (mg P/L)	P Adsorbed, C_{ab} (mg P/L)	% Removal	Q (mg P/g WTRS)	C_e/Q (g/L)
1.78	1	0.15	1.63	91.8	3.20	0.05
	2	0.21	1.57	88.3	3.07	0.07
	3	0.21	1.57	88.3	3.07	0.07
2.37	1	0.49	1.88	79.4	3.69	0.13
	2	0.38	1.99	83.8	3.89	0.10
	3	0.42	1.95	82.4	3.83	0.11
3.56	1	0.94	2.62	73.6	5.13	0.18
	2	0.94	2.62	73.6	5.13	0.18
	3	0.94	2.62	73.6	5.13	0.18

Table C.2 continued

Initial P Concentration, C_o (mg P/L)	Replicate	Equilibrium P Concentration, C_e (mg P/L)	P Adsorbed, C_{ab} (mg P/L)	% Removal	Q (mg P/g WTRS)	C_e/Q (g/L)
4.74	1	1.57	3.18	67.0	6.22	0.25
	2	1.57	3.18	67.0	6.22	0.25
	3	1.78	2.97	62.6	5.81	0.31
5.93	1	2.40	3.53	59.5	6.91	0.35
	2	2.72	3.21	54.2	6.29	0.43
	3	2.93	3.00	50.7	5.88	0.50
7.12	1	3.97	3.15	44.2	6.16	0.64
	2	3.87	3.25	45.7	6.36	0.61
	3	4.28	2.83	39.8	5.54	0.77

Table C.3 Phosphorus adsorption in P-spiked deionized water using Sample 1 Prince Albert WTRS results

Initial P Concentration, C_o (mg P/L)	Replicate	Equilibrium P Concentration, C_e (mg P/L)	P Adsorbed, C_{ab} (mg P/L)	% Removal	Q (mg P/g WTRS)	C_e/Q (g/L)
2.02	1	0.31	1.70	84.5	33.38	0.009
	2	0.13	1.89	93.8	37.06	0.003
	3	0.11	1.90	94.3	37.27	0.003
2.37	1	0.31	2.06	86.8	40.35	0.008
	2	0.40	1.98	83.3	38.71	0.010
	3	0.32	2.05	86.3	40.15	0.008
	4	0.26	2.11	89.0	41.38	0.006
2.97	1	0.83	2.14	72.2	41.94	0.020
	2	0.57	2.39	80.6	46.85	0.012
	3	0.62	2.35	79.2	46.04	0.013
3.56	1	1.21	2.35	65.9	45.98	0.026
	2	1.27	2.28	64.2	44.76	0.028
	3	1.30	2.26	90.9	44.35	0.029
	4	1.50	2.05	57.7	40.25	0.037
4.74	1	2.22	2.53	53.3	49.57	0.045
	2	2.40	2.34	49.3	45.88	0.052
	3	1.99	2.76	58.1	54.08	0.037
	4	2.35	2.39	50.4	46.91	0.050
5.93	1	3.51	2.42	40.8	47.42	0.074
	2	3.41	2.52	42.6	49.47	0.069
	3	3.24	2.69	45.4	52.74	0.061
	4	3.64	2.29	38.7	44.96	0.081
7.12	1	4.28	2.83	39.8	55.51	0.077
	2	4.39	2.73	38.3	53.46	0.082
	3	4.24	2.87	40.4	56.33	0.075

Table C.4 Phosphorus adsorption in P-spiked deionized water using Sample 2 Prince Albert WTRS results

Initial P Concentration, C_o (mg P/L)	Replicate	Equilibrium P Concentration, C_e (mg P/L)	P Adsorbed, C_{ab} (mg P/L)	% Removal	Q (mg P/g WTRS)	C_e/Q (g/L)
2.37	1	0.21	2.16	78.0	42.41	0.005
	2	0.24	2.13	84.6	41.73	0.006
	3	0.28	2.09	80.2	41.05	0.007
2.97	1	0.57	2.39	68.3	46.87	0.012
	2	0.68	2.29	68.3	44.82	0.015
	3	0.68	2.29	66.5	44.82	0.015
3.56	1	0.84	2.72	67.7	53.38	0.016
	2	0.84	2.72	70.6	53.38	0.016
	3	0.94	2.62	70.6	51.33	0.018
4.74	1	1.57	3.18	60.4	62.29	0.025
	2	1.57	3.18	62.6	62.29	0.025
	3	1.67	3.07	62.6	60.24	0.028
5.93	1	2.61	3.32	43.6	65.06	0.040
	2	2.61	3.32	48.9	65.06	0.040
	3	2.72	3.21	43.6	63.01	0.043

Table C.5 Phosphorus adsorption in P-spiked deionized water using Sample 1 Buffalo Pound WTRS results

Initial P Concentration, C_o (mg P/L)	Replicate	Equilibrium P Concentration, C_e (mg P/L)	P Adsorbed, C_{ab} (mg P/L)	% Removal	Q (mg P/g WTRS)	C_e/Q (g/L)
2.37	1	0.19	2.18	92.1	62.18	0.003
	2	0.17	2.20	93.0	62.77	0.003
	3	0.21	2.16	91.2	61.58	0.003
2.73	1	0.38	2.35	86.2	66.95	0.006
	2	0.40	2.33	85.4	66.36	0.006
	3	0.40	2.33	85.4	66.36	0.006
3.20	1	0.73	2.47	77.2	70.35	0.010
	2	0.79	2.41	75.2	68.56	0.012
	3	0.78	2.42	75.5	68.86	0.011
3.56	1	1.26	2.29	64.5	65.30	0.019
	2	1.19	2.37	66.5	67.39	0.018
	3	1.06	2.50	70.3	71.25	0.015
4.74	1	2.08	2.66	56.2	75.86	0.027
	2	2.06	2.69	56.6	76.46	0.027
	3	2.11	2.63	55.5	74.97	0.028

Table C.5 continued

Initial P Concentration, C_o (mg P/L)	Replicate	Equilibrium P Concentration, C_e (mg P/L)	P Adsorbed, C_{ab} (mg P/L)	% Removal	Q (mg P/g WTRS)	C_e/Q (g/L)
5.93	1	3.30	2.63	44.3	74.82	0.044
	2	3.20	2.73	46.1	77.80	0.041
	3	3.43	2.50	42.2	71.25	0.048
7.12	1	4.33	2.79	39.2	79.43	0.054
	2	4.41	2.71	38.0	77.05	0.057

Table C.6 Phosphorus adsorption in P-spiked deionized water using Sample 2 Buffalo Pound WTRS results

Initial P Concentration, C_o (mg P/L)	Replicate	Equilibrium P Concentration, C_e (mg P/L)	P Adsorbed, C_{ab} (mg P/L)	% Removal	Q (mg P/g WTRS)	C_e/Q (g/L)
2.37	1	0.52	1.85	78.0	51.59	0.010
	2	0.37	2.01	84.6	55.97	0.007
	3	0.47	1.90	80.2	53.05	0.009
2.97	1	0.94	2.02	68.3	56.48	0.017
	2	0.94	2.02	68.3	56.48	0.017
	3	0.99	1.97	66.5	55.02	0.018
3.56	1	1.15	2.41	67.7	67.19	0.017
	2	1.05	2.51	70.6	70.10	0.015
	3	1.05	2.51	70.6	70.10	0.015
4.74	1	1.88	2.86	60.4	79.87	0.024
	2	1.78	2.97	62.6	82.78	0.021
	3	1.78	2.97	62.6	82.78	0.021
5.93	1	3.34	2.59	43.6	72.14	0.046
	2	3.03	2.90	48.9	80.89	0.037
	3	3.34	2.59	43.6	72.14	0.046

Table C.7 ANOVA of Saskatoon Sample 1 WTRS isotherm replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.16	3	0.05	0.04	0.99	3.07
Q	30.99	21	1.48			
Total	31.15	24				

Note: Saskatoon Sample 1 isotherm replicates statistically similar

Table C.8 ANOVA of Saskatoon Sample 2 WTRS isotherm replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.40	2	0.20	0.11	0.90	3.68
Q	27.71	15	1.85			
Total	28.11	17				

Note: Saskatoon Sample 2 isotherm replicates statistically similar

Table C.9 ANOVA of Saskatoon Sample 1 and Sample 2 isotherm replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.57	6	0.10	0.06	1.00	2.36
Q	58.71	36	1.63			
Total	59.28	42				

Note: Saskatoon Sample 1 and Sample 2 isotherms statistically similar

Table C.10 ANOVA of Prince Albert Sample 1 WTRS isotherm replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	43.39	3	14.46	0.36	0.78	3.07
Q	850.12	21	40.48			
Total	893.51	24				

Note: Prince Albert Sample 1 isotherm replicates statistically similar

Table C.11 ANOVA of Prince Albert Sample 2 WTRS isotherm replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	9.70	2	4.85	0.05	0.95	3.89
Q	1161.96	12	96.83			
Total	1171.66	14				

Note: Prince Albert Sample 2 isotherm replicates statistically similar

Table C.12 ANOVA of Prince Albert Sample 1 and Sample 2 isotherm replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	622.19	6	103.70	1.70	0.15	2.39
Q	2012.08	33	60.97			
Total	2634.26	39				

Note: Prince Albert Sample 1 and Sample 2 isotherms statistically similar

Table C.13 ANOVA of Buffalo Pound Sample 1 WTRS isotherm replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	13.17	2	6.59	0.20	0.82	3.59
Q	564.50	17	33.21			
Total	577.67	19				

Note: Buffalo Pound Sample 1 WTRS isotherm replicates statistically similar

Table C.14 ANOVA of Buffalo Pound Sample 2 WTRS isotherm replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	37.67	2	18.83	0.12	0.88	3.89
Q	1809.83	12	150.82			
Total	1847.50	14				

Note: Buffalo Pound Sample 2 WTRS isotherm replicates statistically similar

Table C.15 ANOVA of Buffalo Pound Sample 1 and Sample 2 isotherm replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	137.12	5	27.42	0.33	0.89	2.55
Q	2374.33	29	81.87			
Total	2511.44	34				

Note: Buffalo Pound Sample 1 and Sample 2 isotherms statistically similar

APPENDIX D

Phosphorus Adsorption in Municipal Primary Wastewater Effluent Results

Table D.1 Blank phosphorus adsorption results in municipal primary wastewater effluent

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		7.92	8.46
1	1	9.51	10.45
	2	9.61	10.35
	3	9.61	10.45
2	1	9.51	10.66
	2	9.41	10.35
	3	9.72	10.45
3	1	9.09	9.93
	2	9.09	9.82
	3	9.20	10.03
16	1	8.99	9.51
	2	8.67	9.30
	3	9.20	10.14
17	1	9.09	10.87
	2	8.88	9.51
	3	9.51	9.93

Note: Solution remixed on Day 15

Table D.2 Objective based Saskatoon WTRS dosage phosphorus adsorption results in municipal primary wastewater effluent

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		7.92	8.46
1	1	2.61	3.14
	2	2.61	3.87
	3	3.45	4.28
2	1	2.09	2.72
	2	2.19	3.03
	3	2.72	3.55
3	1	1.46	1.67
	2	1.67	1.99
	3	1.67	2.09
7	1	1.05	1.25
	2	1.05	1.25
	3	1.05	1.25
9	1	1.15	1.25
	2	1.25	1.46
	3	1.46	1.57
11	1	1.15	1.25
	2	1.15	1.46
	3	1.57	1.78

Table D.2 continued

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
16	1	0.24	0.21*
	2	0.16	0.10*
	3	0.24	0.21*
17	1	0.39	0.50
	2	0.34	0.37
	3	0.34	0.47
21	1	0.55	0.76
	2	0.52	0.73
	3	0.52	0.73

Note: Solution remixed on Day 15
* Data points removed

Table D.3 Half Saskatoon WTRS dosage phosphorus adsorption results in municipal primary wastewater effluent

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		7.92	8.46
1	1	6.48	7.21
	2	6.48	7.32
	3	6.90	7.42
2	1	6.27	7.11
	2	6.58	7.42
	3	6.79	7.21
3	1	6.06	7.00
	2	6.17	7.11
	3	7.21	7.94
7	1	6.58	7.52
	2	6.37	7.21
	3	7.52	8.05
9	1	6.58	7.21
	2	6.58	7.21
	3	6.58	7.21
11	1	6.27	7.00
	2	6.58	7.63
	3	5.96	6.90
16	1	2.19	2.93
	2	2.30	2.82
	3	1.25	1.46
17	1	2.61	3.03
	2	2.72	3.34
	3	1.46	1.57

Table D.3 continued

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
21	1	2.09	2.61
	2	2.19	2.82
	3	1.25	1.36

Note: Solution remixed on Day 15

Table D.4 Objective based Prince Albert WTRS dosage phosphorus adsorption results in municipal primary wastewater effluent

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		7.92	8.46
0.5	1	4.18	5.12
	2	4.28	5.02
	3	4.60	5.43
1	1	3.97	4.60
	2	4.18	4.49
	3	4.18	5.02
2	1	2.93	3.55
	2	2.93	3.76
	3	3.14	4.49
3	1	2.40	3.24
	2	2.40	3.24
	3	2.93	3.87
4	1	1.88	2.72
	2	1.99	2.93
	3	2.30	3.14
6	1	1.78	2.51
	2	1.99	2.61
	3	2.09	2.82
8	1	1.78	1.99
	2	1.78	2.19
	3	1.99	2.40
14	1	1.57	1.88
	2	1.67	2.09
	3	1.67	2.09
16	1	1.57	1.88
	2	1.57	1.99
	3	1.67	2.09
20	1	1.67	1.88
	2	1.78	1.99
	3	1.57	1.78

Table D.4 continued

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
24	1	1.46	1.78
	2	1.46	1.67
	3	1.57	1.78
29	1	1.05	1.25
	2	0.84	1.25
	3	1.15	1.46
30	1	0.84	1.05
	2	0.84	1.05
	3	1.05	1.52
31	1	0.84	1.05
	2	0.73	0.94
	3	0.94	1.25
35	1	0.73	0.94
	2	0.63	0.84
	3	0.73	0.94

Note: Solution remixed on Day 28

Table D.5 Half Prince Albert WTRS dosage phosphorus adsorption results in municipal primary wastewater effluent

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		7.92	8.46
0.5	1	7.00	7.84
	2	7.32	8.05
	3	7.11	8.05
1	1	6.69	7.11
	2	6.79	7.73
	3	6.37	7.42
2	1	5.64	6.27
	2	5.75	6.69
	3	5.85	6.37
3	1	4.39	5.02
	2	4.60	5.33
	3	4.60	5.54
4	1	3.45	4.49
	2	3.66	5.33
	3	4.18	5.23
6	1	4.18	4.91
	2	4.49	5.12
	3	4.18	5.33

Table D.5 continued

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
8	1	4.39	5.12
	2	4.70	5.33
	3	4.49	5.23
14	1	4.49	5.43
	2	4.70	6.06
	3	4.60	5.23
20	1	4.81	5.23
	2	5.23	5.96
	3	4.39	4.91
22	1	4.18	5.23
	2	4.49	5.43
	3	4.39	5.33
23	1	4.39	4.81
	2	4.60	5.43
	3	4.28	5.43
27	1	3.97	4.91
	2	4.60	5.64
	3	3.97	5.33

Note: Solution remixed on Day 20 after sampling

Table D.6 Exceeding Prince Albert WTRS dosage phosphorus adsorption results in municipal primary wastewater effluent

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		7.92	8.46
1	1	1.05	1.25
	2	1.25	1.46
	3	1.05	1.25
2	1	0.96	1.34
	2	0.79	1.09
	3	0.71	1.05
3	1	0.75	1.05
	2	0.63	0.71
	3	0.59	0.63
7	1	0.46	0.63
	2	0.08*	0.17*
	3	0.04*	0.08*
9	1	0.40	0.59
	2	0.25	0.40
	3	0.21	0.33

Table D.6 continued

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
11	1	0.33	0.40
	2	0.29	0.40
	3	0.27	0.38
16	1	0.13	0.15
	2	0.13	0.17
	3	0.10	0.17
17	1	0.13	0.17
	2	0.13	0.15
	3	0.10	0.19
21	1	0.15	0.17
	2	0.10	0.17
	3	0.10	0.15

Note: Solution remixed on Day 15
* Data points removed

Table D.7 Objective based Buffalo Pound WTRS dosage phosphorus adsorption results in municipal primary wastewater effluent

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		7.92	8.46
0.5	1	5.43	6.06
	2	5.12	6.06
	3	5.43	6.27
1	1	5.12	5.85
	2	4.91	5.64
	3	5.02	5.96
2	1	4.18	4.91
	2	4.18	5.54
	3	3.97	5.33
3	1	3.45	4.08
	2	3.76	4.60
	3	3.34	4.08
4	1	2.61	3.87
	2	3.03	4.08
	3	2.72	3.34
6	1	2.19	2.82
	2	2.51	3.14
	3	2.09	2.93
8	1	1.99	2.40
	2	2.09	2.51
	3	1.99	2.51

Table D.7 continued

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
10	1	1.78	2.30
	2	1.88	2.51
	3	1.78	2.19
14	1	1.57	1.99
	2	1.57	1.88
	3	1.46	1.88
16	1	1.57	1.88
	2	1.57	1.78
	3	1.57	1.78
20	1	1.46	1.57
	2	1.57	1.78
	3	1.36	1.46
24	1	1.46	1.78
	2	1.25	1.46
	3	1.25	1.46
29	1	0.94	1.25
	2	0.84	1.05
	3	0.84	1.15
30	1	0.94	1.10
	2	0.73	0.99
	3	0.73	0.99
31	1	0.94	1.05
	2	0.73	0.94
	3	0.73	1.05

Note: Solution remixed on Day 28

Table D.8 Half Buffalo Pound WTRS dosage phosphorus adsorption results in municipal primary wastewater effluent

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		7.92	8.46
0.5	1	7.63	8.05
	2	6.48	7.11
	3	7.32	7.94
1	1	6.90	8.05
	2	6.58	7.52
	3	6.48	7.52
2	1	5.85	6.69
	2	5.64	6.17
	3	5.54	6.27

Table D.8 continued

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
3	1	5.02	5.85
	2	5.23	5.96
	3	4.39	5.43
4	1	4.81	5.23
	2	4.39	5.75
	3	4.18	5.43
6	1	4.49	5.23
	2	4.28	5.64
	3	4.08	5.33
8	1	4.60	5.23
	2	4.49	5.23
	3	4.18	4.91
10	1	4.39	5.54
	2	4.28	5.43
	3	4.49	5.54
14	1	4.49	5.43
	2	4.18	5.23
	3	3.87	4.39
20	1	4.60	5.33
	2	4.28	4.70
	3	4.08	4.91
22	1	4.28	5.12
	2	3.87	5.12
	3	4.39	5.33
23	1	4.39	4.81
	2	3.55	4.70
	3	4.08	5.12
27	1	3.97	4.91
	2	3.34	4.81
	3	3.76	5.02

Note: Solution remixed on Day 20 after sampling

Table D.9 Exceeding Buffalo Pound WTRS dosage phosphorus adsorption results in municipal primary wastewater effluent

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		7.92	8.46
1	1	1.99	3.03
	2	1.88	2.82
	3	1.99	2.61

Table D.9 continued

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
2	1	2.17	2.63
	2	2.34	2.55
	3	2.05	2.68
3	1	1.25	1.46
	2	1.36	1.57
	3	1.05	1.25
7	1	0.52	0.73
	2	0.42	0.63
	3	0.42	0.63
9	1	0.59	0.79
	2	0.54	2.22*
	3	0.54	0.75
11	1	0.50	0.71
	2	0.54	0.67
	3	0.50	0.67
16	1	0.13	0.21
	2	0.17	0.25
	3	0.13	0.21
17	1	0.13	0.18
	2	0.13	0.24
	3	0.16	0.24
21	1	0.16	0.21
	2	0.10	0.18
	3	0.13	0.21

Note: Solution remixed on Day 15
* Data points removed

Table D.10 Turbidity of blank municipal primary wastewater effluent

Day	Replicate	Turbidity (NTU)
0.5	1	64.4
	2	90.0
	3	79.8
1	1	65.4
	2	81.0
	3	66.4
2	1	74.0
	2	33.5
	3	64.6
3	1	24.7
	2	18.8
	3	27.3

Table D.10 continued

Day	Replicate	Turbidity (NTU)
7	1	15.0
	2	12.7
	3	16.1
9	1	12.5
	2	27.0
	3	17.5
11	1	13.1
	2	9.83
	3	31.1
16	1	9.64
	2	9.46
	3	7.03
17	1	8.34
	2	7.63
	3	4.68
19	1	2.01
	2	2.81
	3	2.07

Table D.11 Turbidity of municipal primary wastewater effluent treated with Saskatoon WTRS objective based dosage

Day	Replicate	Turbidity (NTU)
0.5	1	85.0
	2	57.3
	3	55.1
1	1	43.5
	2	44.2
	3	29.7
2	1	47.0
	2	38.4
	3	26.8
3	1	58.8
	2	49.4
	3	32.7
7	1	77.2
	2	67.2
	3	51.7
9	1	69.9
	2	51.1
	3	36.5
11	1	54.5
	2	44.7
	3	20.0

Table D.11 continued

Day	Replicate	Turbidity (NTU)
16	1	27.8
	2	37.6
	3	19.0
17	1	25.9
	2	35.4
	3	17.1
19	1	19.2
	2	26.8
	3	13.7

Table D.12 Turbidity of municipal primary wastewater effluent treated with Saskatoon WTRS half dosage

Day	Replicate	Turbidity (NTU)
0.5	1	59.9
	2	63.2
	3	70.7
1	1	33.6
	2	32.7
	3	40.3
2	1	35.9
	2	34.0
	3	30.6
3	1	39.7
	2	36.7
	3	34.4
7	1	23.6
	2	18.3
	3	14.1
9	1	21.4
	2	19.7
	3	9.59
11	1	19.5
	2	17.0
	3	9.66
16	1	22.1
	2	23.9
	3	28.3
17	1	19.2
	2	21.9
	3	22.0
19	1	13.6
	2	10.3
	3	11.1

Table D.13 Turbidity of municipal primary wastewater effluent treated with Prince Albert WTRS objective based dosage

Day	Replicate	Turbidity (NTU)
0.5	1	36.1
	2	36.8
	3	14.6
1	1	25.0
	2	25.5
	3	11.3
2	1	22.1
	2	22.1
	3	8.64
3	1	13.7
	2	15.8
	3	11.7
4	1	9.88
	2	8.40
	3	16.7
6	1	5.28
	2	5.28
	3	6.12
8	1	5.93
	2	5.93
	3	5.47
10	1	6.39
	2	6.27
	3	3.84
14	1	4.80
	2	3.21
	3	2.76
16	1	3.51
	2	2.98
	3	2.40
20	1	3.03
	2	3.43
	3	2.57
24	1	2.42
	2	3.11
	3	2.03
29	1	4.02
	2	3.98
	3	4.78
30	1	3.40
	2	3.15
	3	4.04

Table D.13 continued

Day	Replicate	Turbidity (NTU)
31	1	3.12
	2	2.86
	3	3.68
35	1	2.16
	2	2.19
	3	2.71

Table D.14 Turbidity of municipal primary wastewater effluent treated with Prince Albert WTRS half dosage

Day	Replicate	Turbidity (NTU)
0.5	1	56.9
	2	56.8
	3	44.9
1	1	49.6
	2	46.9
	3	37.5
2	1	31.6
	2	28.4
	3	28.5
3	1	31.4
	2	29.1
	3	25.3
4	1	26.4
	2	25.2
	3	14.4
6	1	12.4
	2	13.4
	3	6.48
8	1	15.9
	2	9.94
	3	6.23
10	1	6.19
	2	9.96
	3	5.09
14	1	5.80
	2	6.18
	3	3.29
16	1	5.73
	2	5.41
	3	3.47
20	1	4.11
	2	2.97
	3	2.62

Table D.14 continued

Day	Replicate	Turbidity (NTU)
21.5	1	5.94
	2	5.89
	3	5.18
22	1	5.63
	2	4.75
	3	4.48
23	1	4.92
	2	3.89
	3	4.05
27	1	2.51
	2	3.00
	3	2.60

Table D.15 Turbidity of municipal primary wastewater effluent treated with Prince Albert WTRS exceeding dosage

Day	Replicate	Turbidity (NTU)
0.5	1	9.99
	2	68.2
	3	88.3
1	1	11.2
	2	94.4
	3	95.6
2	1	8.43
	2	126
	3	136
3	1	8.08
	2	19.5
	3	18.3
7	1	2.90
	2	8.43
	3	11.8
9	1	2.79
	2	3.36
	3	12.8
11	1	2.05
	2	2.78
	3	13.0
16	1	4.84
	2	2.37
	3	2.22
17	1	3.46
	2	1.98
	3	1.81

Table D.15 continued

Day	Replicate	Turbidity (NTU)
19	1	2.23
	2	1.76
	3	1.78

Table D.16 Turbidity of municipal primary wastewater effluent treated with Buffalo Pound WTRS objective based dosage

Day	Replicate	Turbidity (NTU)
0.5	1	21.9
	2	8.30
	3	18.4
1	1	17.7
	2	7.67
	3	13.0
2	1	9.99
	2	7.16
	3	9.42
3	1	8.05
	2	7.71
	3	8.85
4	1	6.86
	2	9.43
	3	8.74
6	1	6.35
	2	6.42
	3	6.75
8	1	5.60
	2	12.8
	3	5.75
10	1	12.6
	2	4.53
	3	10.3
14	1	3.52
	2	2.76
	3	3.16
16	1	3.55
	2	2.67
	3	3.28
20	1	2.34
	2	2.05
	3	2.23
24	1	2.59
	2	1.67
	3	2.48

Table D.16 continued

Day	Replicate	Turbidity (NTU)
29	1	2.87
	2	2.97
	3	4.07
30	1	2.34
	2	2.12
	3	3.56
31	1	2.13
	2	1.89
	3	2.97

Table D.17 Turbidity of municipal primary wastewater effluent treated with Buffalo Pound WTRS half dosage

Day	Replicate	Turbidity (NTU)
0.5	1	62.0
	2	52.2
	3	55.3
1	1	44.5
	2	34.8
	3	41.1
2	1	34.1
	2	28.4
	3	33.3
3	1	29.7
	2	14.3
	3	29.2
4	1	21.9
	2	8.81
	3	20.0
6	1	10.2
	2	11.7
	3	11.9
8	1	8.33
	2	4.03
	3	10.4
10	1	8.20
	2	3.93
	3	7.41
14	1	4.96
	2	2.23
	3	3.66
16	1	3.73
	2	2.13
	3	2.83

Table D.17 continued

Day	Replicate	Turbidity (NTU)
20	1	3.04
	2	2.18
	3	2.01
21.5	1	3.95
	2	3.82
	3	3.76
22	1	3.85
	2	3.53
	3	3.29
23	1	3.86
	2	3.52
	3	2.99
27	1	2.07
	2	3.38
	3	2.46

Table D.18 Turbidity of municipal primary wastewater effluent treated with Buffalo Pound WTRS exceeding dosage

Day	Replicate	Turbidity (NTU)
0.5	1	68.7
	2	86.7
	3	81.5
1	1	72.2
	2	98.5
	3	94.9
2	1	66.8
	2	92.5
	3	75.5
3	1	20.8
	2	16.5
	3	15.8
7	1	11.9
	2	10.6
	3	10.6
9	1	15.2
	2	28.8
	3	36.8
11	1	33.2
	2	7.90
	3	11.0
16	1	8.08
	2	6.02
	3	7.21

Table D.18 continued

Day	Replicate	Turbidity (NTU)
17	1	7.34
	2	5.90
	3	6.98
19	1	2.02
	2	5.30
	3	3.06

Table D.19 pH of WTRS treated municipal primary wastewater effluent

Day	Blank	Saskatoon Objective based Replicate 1	Prince Albert Objective based Replicate 1	Prince Albert Half Replicate 1
0	8.43	8.43	8.43	8.43
0.5	-	-	8.26	8.37
1	8.62	8.55	8.37	8.34
2	8.44	8.45	8.32	8.65
3	8.47	8.55	8.54	-
4	-	-	8.53	-
6	-	-	8.69	8.54
7	8.67	8.65	-	-
8	-	-	8.61	-
9	8.68	8.72	-	-
10	-	-	8.71	8.53
11	8.58	8.55	-	-
14	-	-	8.61	8.60
16	8.65	8.66	8.70	8.72
17	8.68	8.66	-	-
20	-	-	8.69	8.69
21	8.61	8.61	-	-
21.5	-	-	-	8.71
23	-	-	-	8.64
24	-	-	8.46	-
27	-	-	-	8.62
29	-	-	8.06	-
30	-	-	8.09	-
31	-	-	8.07	-

Table D.20 ANOVA of orthophosphate blank dosage replicates (α = 0.05)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.25	2	0.13	1.43	0.28	3.89
P Conc.	1.07	12	0.09			
Total	1.32	14				

Note: Blank replicates statistically similar

Table D.21 ANOVA of total phosphorus blank dosage replicates (α = 0.05)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.49	2	0.24	1.24	0.33	3.89
P Conc.	2.38	12	0.20			
Total	2.87	14				

Note: Blank replicates statistically similar

Table D.22 ANOVA of orthophosphate Saskatoon WTRS objective based dosage replicates (α = 0.05)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.36	2	0.18	0.22	0.81	3.40
P Conc.	19.81	24	0.83			
Total	20.17	26				

Note: Saskatoon WTRS objective based dosage replicates statistically similar

Table D.23 ANOVA of total phosphorus Saskatoon WTRS objective based dosage replicates (α = 0.05)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.63	2	0.32	0.24	0.79	3.47
P Conc.	27.80	21	1.32			
Total	28.43	23				

Note: Saskatoon WTRS objective based dosage replicates statistically similar

Table D.24 ANOVA of orthophosphate Saskatoon WTRS half dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.08	2	0.03	0.01	0.99	3.40
P Conc.	128.89	24	5.37			
Total	128.95	26				

Note: Saskatoon WTRS half dosage replicates statistically similar

Table D.25 ANOVA of total phosphorus Saskatoon half dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.93	2	0.46	0.07	0.93	3.40
P Conc.	154.09	24	6.42			
Total	155.02	26				

Note: Saskatoon WTRS half dosage replicates statistically similar

Table D.26 ANOVA of orthophosphate Prince Albert WTRS objective based dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.33	2	0.17	0.13	0.87	3.22
P Conc.	52.01	42	1.24			
Total	52.34	44				

Note: Prince Albert WTRS objective based dosage replicates statistically similar

Table D.27 ANOVA of total phosphorus Prince Albert WTRS objective based dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.85	2	0.42	0.24	0.79	3.22
P Conc.	73.95	42	1.76			
Total	74.80	44				

Note: Prince Albert WTRS objective based dosage replicates statistically similar

Table D.28 ANOVA of orthophosphate Prince Albert WTRS half dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.50	2	0.25	0.23	0.80	3.28
P Conc.	36.18	33	1.10			
Total	36.68	35				

Note: Prince Albert WTRS half dosage replicates statistically similar

Table D.29 ANOVA of total phosphorus Prince Albert WTRS half dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	1.38	2	0.69	0.70	0.50	3.28
P Conc.	32.55	33	0.99			
Total	33.93	35				

Note: Prince Albert WTRS half dosage replicates statistically similar

Table D.30 ANOVA of orthophosphate Prince Albert WTRS exceeding dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.04	2	0.02	0.13	0.88	3.44
P Conc.	3.07	22	0.14			
Total	3.10	24				

Note: Prince Albert WTRS exceeding dosage replicates statistically similar

Table D.31 ANOVA of total phosphorus Prince Albert WTRS exceeding dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.06	2	0.03	0.14	0.87	3.44
P Conc.	4.68	22	0.21			
Total	4.74	24				

Note: Prince Albert WTRS exceeding dosage replicates statistically similar

Table D.32 ANOVA of orthophosphate Buffalo Pound WTRS objective based dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.09	2	0.04	0.02	0.98	3.22
P Conc.	93.90	42	2.24			
Total	93.99	44				

Note: Buffalo Pound WTRS objective based dosage replicates statistically similar

Table D.33 ANOVA of total phosphorus Buffalo Pound WTRS objective based dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.08	2	0.04	0.01	0.99	3.22
P Conc.	130.93	42	3.12			
Total	131.01	44				

Note: Buffalo Pound WTRS objective based dosage replicates statistically similar

Table D.34 ANOVA of orthophosphate Buffalo Pound WTRS half dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	1.14	2	0.57	0.50	0.61	3.26
P Conc.	41.27	36	1.15			
Total	42.40	38				

Note: Buffalo Pound WTRS half dosage replicates statistically similar

Table D.35 ANOVA of total phosphorus Buffalo Pound WTRS half dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.25	2	0.12	0.12	0.89	3.26
P Conc.	36.55	36	1.02			
Total	36.80	38				

Note: Buffalo Pound WTRS half dosage replicates statistically similar

Table D.36 ANOVA of orthophosphate Buffalo Pound WTRS exceeding dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.02	2	0.01	0.02	0.98	3.40
P Conc.	15.11	24	0.63			
Total	15.13	26				

Note: Buffalo Pound WTRS exceeding dosage replicates statistically similar

Table D.37 ANOVA of total phosphorus Buffalo Pound WTRS exceeding dosage replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.04	2	0.02	0.02	0.98	3.42
P Conc.	24.63	23	1.07			
Total	24.67	25				

Note: Buffalo Pound WTRS exceeding dosage replicates statistically similar

APPENDIX E

Phosphorus Adsorption in Agricultural Runoff Pond Water Results

Table E.1 Objective based Saskatoon WTRS dosage phosphorus adsorption results in agricultural runoff pond water

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		1.92	2.86
1	1	1.76	2.26
	2	2.30	2.72
	3	1.92	2.47
2	1	1.55	2.17
	2	2.17	2.84
	3	1.88	2.55
4	1	1.15	1.46
	2	1.57	1.99
	3	1.36	1.78
7	1	1.42	2.05
	2	2.05	2.59
	3	1.76	2.30
8	1	1.30	1.96
	2	2.05	2.55
	3	1.71	2.30
14	1	1.02	1.46
	2	1.49	1.88
	3	1.36	1.65

Note: Solution remixed on Day 7 after sampling and WTRS dosage doubled on Day 13

Table E.2 Objective based Buffalo Pound WTRS dosage phosphorus adsorption results in agricultural runoff pond water

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
0		1.92	2.86
1	1	2.26	2.88
	2	2.01	2.59
	3	2.13	2.76
2	1	2.13	2.76
	2	1.88	2.47
	3	2.05	2.59
4	1	1.46	2.09
	2	1.36	1.88
	3	1.46	1.99
7	1	1.88	2.47
	2	1.59	2.30
	3	1.76	2.42
8	1	1.92	2.47
	2	1.59	2.34
	3	1.80	2.47

Table E.2 continued

Day	Replicate	Orthophosphate (mg P/L)	Total Phosphorus (mg P/L)
14	1	1.33	1.78
	2	1.18	1.59
	3	1.28	1.62

Note: Solution remixed on Day 7 after sampling and WTRS dosage doubled on Day 13

Table E.3 pH of WTRS treated agricultural runoff pond water

Day	Saskatoon Desired Replicate 1
0	8.40
1	8.89
2	8.88
4	8.37
7	8.47
14	8.63

Table E.4 ANOVA of orthophosphate Saskatoon WTRS treated agricultural runoff pond water replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.99	2	0.49	6.06	0.01	3.68
P Conc.	1.22	15	0.08			
Total	2.21	17				

Note: Orthophosphate Saskatoon WTRS agricultural runoff pond water treatment replicates are not statistically similar

Table E.5 Tukey test of orthophosphate Saskatoon WTRS treated agricultural runoff pond water replicates

	A	B	C
Mean	1.36	1.94	1.67
q	3.67		
Honest Significant Difference (HSD)	0.43		
B-A	0.57		
B-C	0.27		
C-A	0.30		

Note: 0.57 (B-A) > 0.43 ∴ A and B different from each other. Although A and B can be considered different from each other, neither data set was removed

Table E.6 ANOVA of total phosphorus Saskatoon WTRS treated agricultural runoff pond water replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.85	2	0.43	3.05	0.08	3.68
P Conc.	2.10	15	0.14			
Total	2.95	17				

Note: Total phosphorus Saskatoon WTRS treated agricultural runoff pond water replicates statistically similar

Table E.7 ANOVA of orthophosphate Buffalo Pound WTRS treated agricultural runoff pond water replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.16	2	0.08	0.73	0.50	3.68
P Conc.	1.69	15	0.11			
Total	1.85	17				

Note: Orthophosphate Buffalo Pound WTRS treated agricultural runoff pond water replicates statistically similar

Table E.8 ANOVA of total phosphorus Buffalo Pound WTRS treated agricultural runoff pond water replicates ($\alpha = 0.05$)

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F crit
Replicate	0.04	2	0.02	0.07	0.93	3.68
P Conc.	3.95	15	0.26			
Total	3.99	17				

Note: Total phosphorus Buffalo Pound WTRS treated agricultural runoff pond water replicates statistically similar

APPENDIX F

Phosphorus Desorption from WTRS Results

Table F.1 Saskatoon WTRS phosphorus desorption results

WTRS Dosage	Replicate	P Sorbed (mg)		P Desorbed (mg)		% Desorbed	
		Ortho P	Total P	Ortho P	Total P	Ortho P	Total P
Desired	1	42.97	46.21	1.23	1.14	2.87	2.46
	2	43.13	46.37	0.74	0.74	1.72	1.60
	3	43.13	46.37	0.72	0.72	1.66	1.54
Half	1	31.85	35.09	1.10	0.63	3.45	1.79
	2	30.59	33.83	0.55	0.45	1.78	1.33
	3	39.37	42.61	1.22	1.19	3.11	2.80
Exceed	1		50.76		0.25		0.49
	2		50.76		0.25		0.49
	3		50.76		0.25		0.49

Note: No data for orthophosphate Saskatoon exceeding dosage

Table F.2 Prince Albert WTRS phosphorus desorption results

WTRS Dosage	Replicate	P Sorbed (mg)		P Desorbed (mg)		% Desorbed	
		Ortho P	Total P	Ortho P	Total P	Ortho P	Total P
Desired	1	41.88	45.12	0.60	0.69	1.43	1.53
	2	42.50	45.74	0.96	1.02	2.25	2.23
	3	41.88	45.12	0.50	0.56	1.18	1.24
Half	1	18.05	21.29	0.65	1.50	3.62	7.05
	2	13.66	16.90	0.54	0.88	3.95	5.23
	3	15.54	18.78	0.34	2.09	2.18	11.15
Exceed	1	46.52	49.76	< 0.05	< 0.05	< 0.05	< 0.05
	2	46.52	49.76	< 0.05	< 0.05	< 0.05	< 0.05
	3	46.64	49.88	< 0.05	< 0.05	< 0.05	< 0.05

Table F.3 Buffalo Pound WTRS phosphorus desorption results

WTRS Dosage	Replicate	P Sorbed (mg)		P Desorbed (mg)		% Desorbed	
		Ortho P	Total P	Ortho P	Total P	Ortho P	Total P
Desired	1	41.25	44.49	0.01	-0.09	0.01	-0.20
	2	41.88	45.12	0.58	0.58	1.38	1.28
	3	41.25	44.49	-0.05	-0.15	-0.13	-0.33
Half	1	31.85	21.29	1.10	2.05	3.45	9.62
	2	30.59	21.92	0.55	2.13	1.78	9.70
	3	39.37	20.66	1.22	2.58	3.11	12.50
Exceed	1	46.27	49.51	< 0.05	< 0.05	< 0.05	< 0.05
	2	46.42	49.66	< 0.05	< 0.05	< 0.05	< 0.05
	3	46.27	49.51	< 0.05	< 0.05	< 0.05	< 0.05